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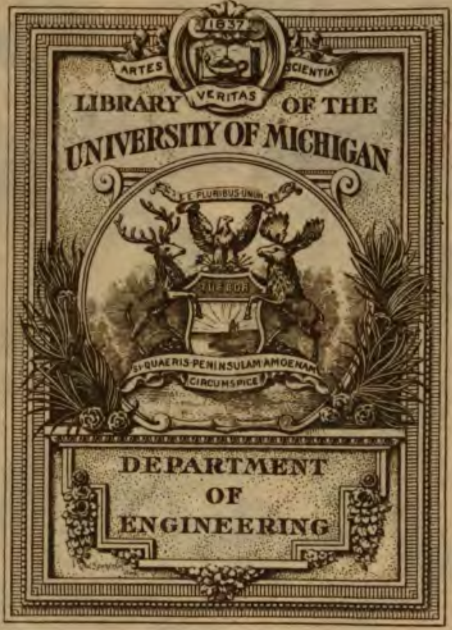

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ENGINEERING APPLICATIONS
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BY

V. KARAPETOFF

PART III.
PROBLEMS ON THERMODYNAMICS

FIRST EDITION
FIRST THOUSAND

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PREFACE TO PART III.

THE third part of the work, now offered to the profession, contains problems in thermodynamics of perfect gases and saturated steam. The first part contains problems in machine design, the second part problems in hydraulics and the remaining two parts are devoted to mechanics of materials and electrical engineering respectively. Thus in using this work a student or an engineer who wishes to review calculus or analytics, or to acquire facility in applications of higher mathematics to engineering problems, may select at first the part of the work which deals with problems in that branch of engineering with which he is most familiar, or in which he is particularly interested.

The book as a whole is not intended to bring out anything new, either in mathematical methods or in practical deductions. The author's aim was simply to collect and to arrange in a systematic way the various applications of analytic geometry and of calculus, already in use. The book may be called a summary of the most common engineering applications of higher mathematics, or a mathematical cross-index to engineering text-books. It fulfills its purpose if it saves the teacher the trouble of consulting many engineering books for the purpose of selecting a few mathematical problems for his students. The author also hopes that the book may stimulate interest in higher mathematics among his fellow engineers and thus help to a better understanding of some intricate relations where at present "rule of thumb" prevails in design.

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The reader will find the author's views on teaching mathematics to engineering students in the preface to Part I and in the Dialogue following that preface. He is also referred to Part I for a list of reference works on mathematics and for an Appendix entitled "What a Senior in Engineering ought to know about Mathematics."

The author wishes to acknowledge gratefully the assistance of his former students, Mr. J. G. Pertsch, M.E., Instructor in Electrical Engineering at Cornell University, who read the manuscript on thermodynamics, and Mr. Fred G. Switzer, M.M.E., who solved most of the problems. Mr. A. C. Stevens, M.E., Instructor in Cornell University, read the proofs, and made a number of valuable suggestions.

Cornell University, Ithaca, N. Y.
January, 1916.

CONTENTS.

CHAPTER PAGE

I. WORK DONE BY EXPANDING A PERFECT GAS............. 3

II. WORK DONE BY EXPANDING A PERFECT GAS (*continued*).. 19

III. PRESSURE-TEMPERATURE CURVES OF SATURATED STEAM... 40

IV. HEAT OF VAPORIZATION AND DENSITY OF SATURATED STEAM 67

V. ENTROPY OF GASES, LIQUIDS, AND VAPORS............... 78

VI. HEAT TRANSFER IN BOILERS 97

LIST OF REFERENCE WORKS............................ 113

PART III.

PROBLEMS ON THERMODYNAMICS.

ENGINEERING MATHEMATICS.

CHAPTER I.

WORK DONE BY EXPANDING A PERFECT GAS.

(a) Fundamental Cases.

THE action of the two most important classes of prime movers, viz., steam engines and gas engines, is based upon the expansion of a gas or a vapor. In the steam engine, the working gas is water and vapor, in the gas engine it is mostly atmospheric air brought to a high temperature and pressure by an admixture of certain explosive gases or vapors. In order therefore to understand the action of these prime movers and be able to calculate their dimensions for the performance of certain work, it is necessary to know some of the properties of gases.

To make the conditions more definite it is customary to consider a unit weight of gas, say a kilogram (or a pound). Then the properties of an arbitrary quantity of the same gas may be deduced by simply multiplying or dividing the results obtained for the unit weight by the number of units of weight contained in the gas under consideration. Thus, for instance, if the total mass of gas contains G units of weight, then the total volume $V = Gv$; total heat $H = Gh$; total work $W = Gw$; etc., where v, h, w, etc., denote the respective quantities per unit weight of gas. For our purposes, a kilogram (or pound) of gas is characterized by three quantities:

(1) volume;
(2) pressure;
(3) temperature.

This is illustrated in Fig. 1: Let one kilogram of a certain gas, for instance, atmospheric air, be comprised in a cylinder C provided with a piston B, pressed down by a total force of P kilograms.* If the cross section of the cylinder, or the area of the piston, is S square meters, then $P/S = p$ represents the pressure of the gas in kilograms per square meter. Let the cylinder be surrounded by a bath so that the gas within is maintained at a constant temperature t. Then the gas will assume a definite volume v. In this sense, it is said that a gas is perfectly defined by two out of its three characteristics, say, by its pressure and temperature.

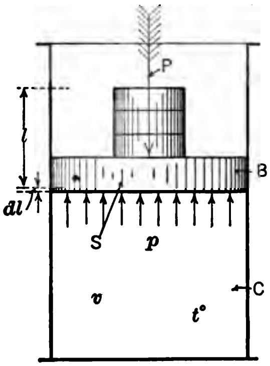

FIG. 1. — Gas compressed in a cylinder.

Before taking up changes in a gas when two of its properties, for instance volume and temperature, are varied at will, let us investigate what happens to the gas when one of its three characteristics is kept constant, while one of the other two properties follows variations dependent upon changes made at will in the remaining characteristic. It will be understood that we shall have in mind only perfect gases, that is, such that are far from their point of liquefaction and which therefore obey the laws of Boyle and of Gay-Lussac.

---

* The absolute pressure P includes the force of atmospheric pressure and the weight of the piston.

Changes at Constant Volume.

Let the temperature of the gas (Fig. 1) be gradually increased by supplying heat from outside; the gas will expand, raising the piston, and in order to keep the volume constant it will be necessary to increase the force *P*. Another way to perform the experiment is to lock the piston in place and to measure the pressure with a pressure-gage, such as is used on steam boilers. Plotting results as shown in Fig. 2, a straight line is obtained, indicating how the pressure increases with the temperature. Producing the lines to their intersection with the *t*-axis, a point is obtained, called the absolute zero, or a temperature at which the gas exerts no pressure whatever. Temperatures counted from this point are called absolute temperatures, and are denoted by *T*, in contradistinction to ordinary Centigrade temperatures denoted by *t*. Experiments on so-called perfect or permanent gases give practically the same value of the absolute zero temperature, namely

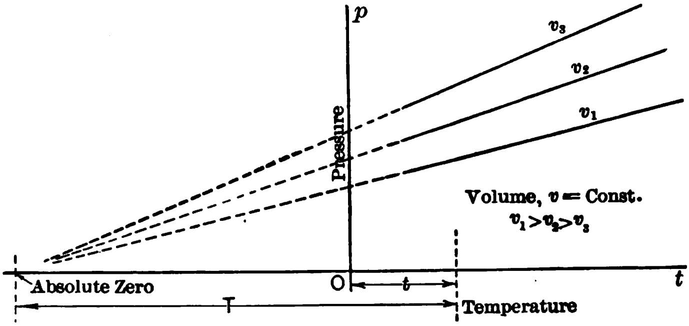

FIG. 2. — Variation of pressure with temperature, at a constant volume.

273° C. below that of freezing water. Thus, for instance, if the temperature $t = 25°$ C., then $T = 25 + 273 = 298°$ C. abs. Fig. 2 shows that, at a constant volume, the pressure in a perfect gas is proportional to the absolute temperature, or

$$p = C_1 T, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_1 depends on the kind of gas and on the unit of volume selected. Experiment shows also that the amount of heat h communicated to the gas per unit of its weight is proportional to the rise in temperature, or

$$h = c_v (t_2 - t_1), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where c_v is the so-called specific heat at constant volume. It will be seen from Eq. (2) that c_v, by definition, is the amount of heat necessary to raise the temperature of one kilogram of gas one degree Centigrade, the volume of the gas remaining constant.

In the metric system the temperatures in Eq. (2) are supposed to be on the Centigrade scale, while heat content h is measured in calories per kilogram weight of gas, one calorie being the amount of heat necessary to raise the temperature of one kilogram mass of water one degree Centigrade, at the temperature of its highest density (between 4 and 5° C.). The specific heat of atmospheric air at constant volume is 0.169. This means that only 16.9 per cent as much heat is necessary to raise the temperature of air as is required to raise the temperature of an equal weight of water an equal number of degrees.

The volume of the vessel being constant, no external work is done by the piston, and all the heat applied is used to raise the temperature of the gas. According to the modern views on the constitution of gases, particles of a gas are in constant motion in all directions (kinetic theory of gases), and an increase in temperature means an increase in the mean velocity of the particles. It is said therefore that the heat supplied in this case increases the intrinsic or internal energy of the gas without producing external work.

Prob. 1. — How much heat is required to raise the temperature of 3 kg. of air 85° C. at a constant volume?

Ans. 43.095 kg-cal.

Changes at Constant Pressure.

Let now the piston (Fig. 1) be loaded with a constant weight P, and let heat be communicated to the gas from the outside; the piston will travel upward, and at the same time the temperature of the gas will increase. The heat supplied is partly converted into the external work of raising the weight, and partly increases the temperature or the intrinsic energy of the gas. Plotting volumes against temperatures, a straight line is obtained (Fig. 3) which intersects the temperature axis at a point corresponding to the absolute zero,

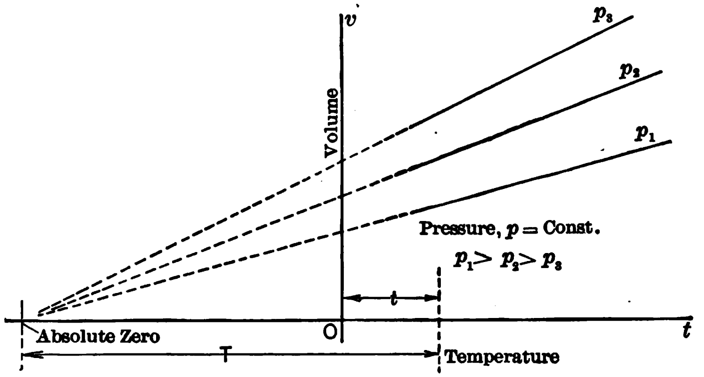

FIG. 3. — Variation of volume with temperature at a constant pressure.

the same as in Fig. 2. Thus, analogously to Eq. (1) we have

$$v = C_2 T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the coefficient of proportionality C_2 depends on the kind of gas and on the pressure used (Gay-Lussac's law).

The heat communicated may be represented here as

$$h = c_p (t_2 - t_1), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where c_p is the specific heat of the gas at constant pressure. It is evident that $c_p > c_v$, because in this case the heat not only raises the temperature of the gas, but also performs some external work. Let the piston rise by an amount l; the total external work performed is then $Pl = pSl = p (v_2 - v_1)$ kg-m.

If volume and pressure are used as abscissæ and ordinates (Fig. 4) the change in the state of the gas is represented by a horizontal line, which shows that the pressure of the gas is independent of its volume. The work $p (v_2 - v_1)$ done by the gas is in this case proportional to the area of the rectangle v_1v_2ba, since its base is $(v_2 - v_1)$ and the altitude represents the pressure p.

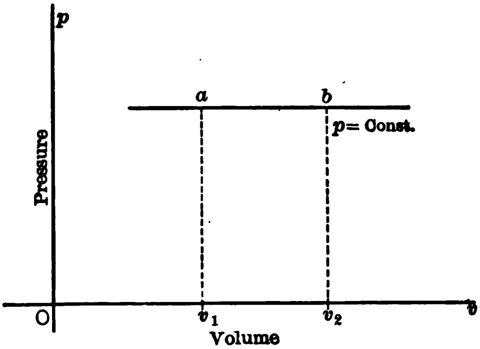

FIG. 4. — Change in volume at a constant pressure.

According to a fundamental law of nature, heat is equivalent to work; that is, in order to perform a certain amount of work, a proportional amount of heat must be used. In the metric system this relation is

$$1 \text{ large calorie} = 427 \text{ kg-m}.$$

It is customary to denote the inverse value of this ratio by A, so that in the metric system

$$A = 1/427.$$

Thus, the amount of heat per unit weight of gas, used in raising the weight P, is

$$Ap\,(v_2 - v_1) \text{ heat units.}$$

On the other hand, the amount of heat necessary to raise the temperature of a perfect gas from t_1 to t_2 is

$$c_v\,(t_2 - t_1),$$

independent of whether the gas is at a constant volume or not.* Hence, the total heat given to the gas is

$$h = c_p\,(t_2 - t_1) = c_v\,(t_2 - t_1) + Ap\,(v_2 - v_1), \quad . \quad (5)$$

where c_p is known as the specific heat at constant pressure.

Prob. 2. — 3 kg. of air at a pressure of 7 metric atmospheres (1 metric atmosphere = 1 kg. per sq. cm.) and at a temperature of 15° C. occupies 0.362 cu. m. The air is allowed to expand at the constant pressure until its volume becomes 0.563 cu. m. It is found that its temperature is 175° C. From these data find how many calories were added to the gas, and what percentage of the heat was used in performing the external work and in increasing the intrinsic energy of the air. Also calculate c_p, knowing that for air $c_v = 0.169$ (in the meter-kilogram system).

---

* This is true of perfect gases only; with imperfect gases part of the heat serves to disintegrate particles of gas and neither raises its temperature nor performs external work. This is called the internal latent heat of the gas. For perfect gases the latent heat is zero, as has been proved by the famous "porous plug" experiment of Joule and Kelvin. Hence, no matter what change of state the gas is undergoing, the increase of its intrinsic energy always corresponds to the increase in temperature, and does not depend upon the volume or pressure.

Ans. 114.06 kg-cal.; 28.88 per cent; 71.12 per cent; $c_p = 0.2375$.

Prob. 3. — In the preceding example, the weight was lifted uniformly in 12 sec. What horse-power was the engine developing during the process? One metric horse-power is equal to 75 kg-m. per sec. *Ans.* 54 metric h.p.

Changes at Constant Temperature.

Let the cylinder (Fig. 1) be a perfect conductor of heat and be surrounded by a very large bath maintained at a constant temperature, so that in whichever way the pressure and volume of the gas may change, its temperature remains constant. Let the gas be in equilibrium occupying a volume v at a pressure p. Remove a small part of the weight P; the piston will be raised upward by a small amount and an equilibrium established again. At the same time a small quantity of heat will flow into the cylinder from the outside to supply the work of lifting the weight. On the other hand, if the weight on the piston is increased, the gas will be compressed, and the work of the weight will be converted into heat. Since the gas is surrounded by a bath maintained at a constant temperature, this extra heat will flow into the surrounding medium. These changes in volume with pressure at a constant temperature are called isothermal changes, and are represented by curves in Fig. 5. Each curve refers to a particular temperature. Experiment shows that under such conditions pressures are inversely proportional to volumes.

Let the initial and the final pressures and volumes of the gas be p_1, p_2 and v_1, v_2 respectively; let some intermediate values be p and v. Then

$$p_1v_1 = pv = p_2v_2 = \text{const.} \quad . \quad . \quad . \quad . \quad (6)$$

The value of the constant depends upon the kind of gas and the temperature at which the experiment is performed (Boyle's law). Eq. (6) represents analytically a family of equilateral hyperbolæ, shown in Fig. 5, each curve corresponding to a certain temperature.

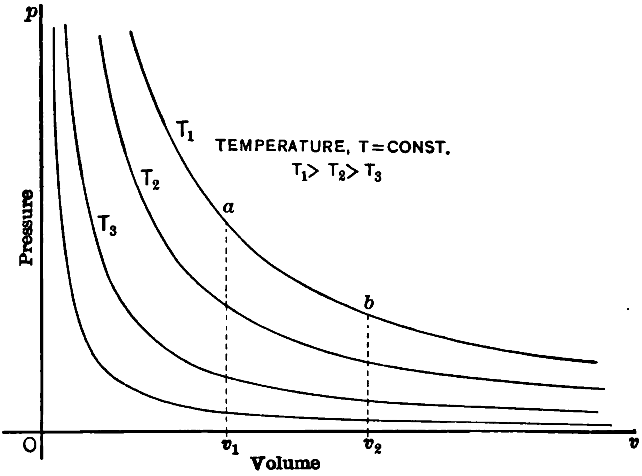

FIG. 5. — Changes in a gas at a constant temperature.

To calculate the work performed in this case it is necessary to integrate over infinitesimal displacements of the piston, because the pressure is different in every position. The work done during an infinitesimal displacement dl is

$$P \cdot dl = pS \cdot dl = p \cdot dv,$$

so that the total work performed, per unit weight of gas, is

$$w = \int_{v_1}^{v_2} p \cdot dv.$$

This work is represented graphically in the p-v diagram (Fig. 5) by the area of the figure v_1v_2ba. This is the reason why pressure and volume are usually selected as coördinates in considering changes in state of substances, since the external work performed is represented by the area of the diagram between the limits of volume.

As the expansion is isothermal and no heat is necessary in perfect gases to disintegrate particles, all the heat supplied is converted into work, and we have, in heat units,

$$h = Aw = A\int_{v_1}^{v_2} p\,dv.$$

Substituting the value of p from Eq. (6) gives

$$w = h/A = p_1v_1\int_{v_1}^{v_2} dv/v = p_1v_1 \operatorname{Ln}(v_2/v_1).^* \quad . \quad (7)$$

From this equation the heat supplied and the work performed may be calculated when the initial conditions of the gas and the limits of expansion are given. If, instead of v_2 and v_1, the limits of pressure p_1 and p_2 are given, the equation becomes

$$w = h/A = p_1v_1 \operatorname{Ln}(p_1/p_2). \quad . \quad . \quad . \quad (8)$$

Prob. 4. — With the initial data given in Prob. 2, assume that the air expands isothermally instead of at a constant pressure. What will be the work performed and the heat supplied; also what is the final pressure of the gas? At what volume and pressure should the expansion begin, in order to get the same mechanical effect as in the case of expansion at a constant pressure of Prob. 2?

Ans. 33,600 kg-m.; 78.6 kg-cal.; 4.5 metric atmos.;
$p_1 = 12.36$ metric atmos.; $v_1 = 0.2047$ cu. m.

Prob. 5. How many kilogram-meters of work are required to compress isothermally 3 kg. of air which originally occupies 425 liters at the temperature of freezing water, to double the original pressure? One kilogram of air occupies a volume of 0.7733 cu. m. at atmospheric pressure and 0° C. Atmospheric pressure = 1.0333 metric atmos. = 1.0333 kg. per sq. cm. *Ans.* 16,500 kg-m.

---

* The symbol Ln is used here to denote the Naperian logarithm; the common logarithm is denoted by the symbol log.

Characteristic Equation of Perfect Gases.

In the preceding processes one of the three characteristics of the gas is considered constant, and the experimental results are expressed by the three equations, (1), (3), and (6). These equations may be combined into

$$pv = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which is called the characteristic equation of a perfect gas. When the volume is constant, the pressure increases as the absolute temperature, as required by Eq. (1); when the pressure is constant, the volume increases proportionately to the absolute temperature, as required by Eq. (3); when the temperature is constant, the product pv is also constant, in accordance with Eq. (6). R is a physical constant which depends on the kind of gas. Its value may be determined from Eq. (9) if a set of corresponding values of p, v, and T is known. For instance, for air, according to Prob. 5, we have at the atmospheric pressure and the temperature of freezing water: $v_0 = 0.7733$ cu. m. per kg.; $T_0 = 0 + 273 = 273°$ C. abs.; $p_0 = 1.0333 \times 10^4 = 10{,}333$ kg. per sq. m. Hence, substituting into (9),

$$R = 10{,}333 \times 0.7733/273 = 29.27.$$

Eq. (9), being a relation between three variables, cannot be represented by a curve, but is represented by a surface shown in Fig. 6. Cross sections by planes corresponding to $v =$ const. give a series of straight lines which represent changes at constant volume, as in Fig. 2. Similarly, cross sections by planes perpendicular to the p-axis give expansions at constant pressure, according to Fig. 3. Intersections with planes perpendicular to the T-axis give equilateral hyperbolæ of isothermal changes, as in Fig. 5.

An excellent idea of the properties of a perfect gas is obtained by actually making a model of the above surface, according to Eq. (9). Planes of coördinates can be made out of wood; isothermal curves are made in the form of ribs out of paste-board, wood, or aluminum; and strings or wires are stretched to represent p-T and v-T lines.*

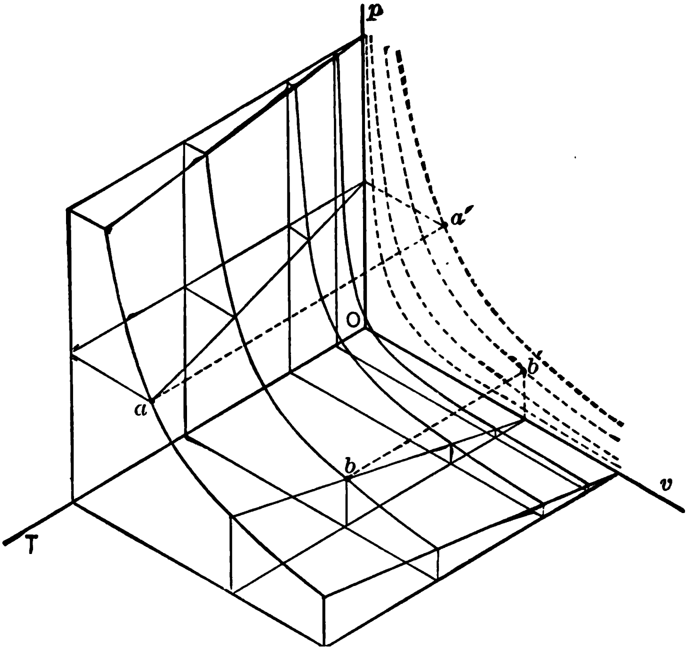

FIG. 6. — A surface showing the relationship between pressure, volume, and temperature in a perfect gas.

A satisfactory picture of the properties of a perfect gas is obtained by projecting isothermals on the *p-v* plane, as in Fig. 6, so that for any p and v, the corresponding temperature, T, may be read directly, or estimated.

---

* Such a model has been constructed by the author. See Sibley Journal of Engineering, Vol. 29 (1914), p. 12.

Prob. 6. — Show by reasoning that the values of R for different gases are inversely as their densities.

Prob. 7. — Prove from Eqs. (5) and (9) that

$$c_p = c_v + AR. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

Adiabatic Expansion.

Besides the processes considered above, when one of the quantities p, v, or T remains constant, there are innumerable other ways of changing the condition of a gas. Among these processes, one that is of particular practical importance is the so-called adiabatic change of state, when no heat is communicated to the gas from outside. Imagine the cylinder and the piston in Fig. 1 to be made of perfect non-conductors of heat; if the pressure on the piston is increased or reduced the gas is compressed or expanded. In expanding it lifts the weight and performs mechanical work. Since no heat is communicated from the outside, this work is done at the expense of the intrinsic energy of the gas itself; consequently, during an adiabatic expansion the gas is cooled. On the contrary, during an adiabatic compression some work is performed upon the gas, and as the mechanical energy thus converted into heat cannot be conducted away, the temperature of the gas rises.

The problem is as follows: being given the original pressure, volume, and temperature of the gas, to find the law according to which they vary during an adiabatic process. As these three quantities are always connected by Eq. (9), only two of them need be determined. Since all the three characteristics of the gas vary continually, it becomes necessary to consider an infinitesimal change. The work $p \cdot dv$, done during such a change, and the consequent decrease of temperature dT are connected by the relationship

$$A \cdot p\,dv = -c_v\,dT \quad . \quad . \quad . \quad . \quad . \quad (11)$$

since the work is done entirely at the expense of the internal energy of the gas. The minus sign before dT is necessary because T decreases when v increases. Eq. (11) may be obtained directly from Eq. (5) by letting $h = 0$ and reducing the interval $t_2 - t_1$ to an infinitesimal.

Eq. (11) is the differential equation of an adiabatic change in a perfect gas; the three variables which enter into it are connected by the characteristic Eq. (9). Hence, eliminating one of the variables between these equations, a relation is obtained between the remaining two variables. It is easy to eliminate p by dividing Eq. (11) by Eq. (9). The result is

$$A\,dv/v = -\,c_v\,dT/RT, \quad . \quad . \quad . \quad . \quad (12)$$

or, integrating,

$$(AR/c_v)\,\mathrm{Ln}\,(v_2/v_1) = \mathrm{Ln}\,(T_1/T_2).$$

Taking into account Eq. (10), this is reduced to

$$\frac{c_p - c_v}{c_v}\,\mathrm{Ln}\left(\frac{v_2}{v_1}\right) = \mathrm{Ln}\left(\frac{T_1}{T_2}\right). \quad . \quad . \quad . \quad (13)$$

The ratio of the specific heats c_p to c_v occurs quite often in the theory of gases and is sometimes denoted by one letter κ, that is,

$$c_p/c_v = \kappa.$$

Eq. (13) becomes

$$(\kappa - 1)\,\mathrm{Ln}\,(v_2/v_1) = \mathrm{Ln}\,(T_1/T_2),$$

or

$$(v_2/v_1)^{\kappa-1} = T_1/T_2. \quad . \quad . \quad . \quad . \quad (14)$$

This is the required relationship between v and T during an adiabatic change. It may be represented in the form

$$T_2 v_2^{\kappa-1} = T_1 v_1^{\kappa-1} = T v^{\kappa-1} = \text{const.} \quad . \quad . \quad . \quad (15)$$

A relationship between p and v is obtained by eliminating T between Eqs. (9) and (15). The result is

$$p_2 v_2^{\kappa} = p_1 v_1^{\kappa} = p v^{\kappa} = \text{const.} \quad . \quad . \quad . \quad (16)$$

Finally, the relationship between p and T is

$$\frac{T_2^{\kappa/(\kappa-1)}}{p_2} = \frac{T_1^{\kappa/(\kappa-1)}}{p_1} = \frac{T^{\kappa/(\kappa-1)}}{p} = \text{const.} \quad . \quad (17)$$

The work of an adiabatic expansion is found directly by integrating Eq. (11), namely

$$Aw = A\int_{v_1}^{v_2} p \cdot dv = -c_v \int_{T_1}^{T_2} dT,$$

or

$$Aw = c_v (T_1 - T_2). \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This result could be easily foreseen, since the work is performed at the expense of the internal energy of the gas. Eq. (18) may be expressed through the volume and the pressure, instead of the temperature, by using Eqs. (9), (15), (16), and (17).

Prob. 8. — Prove that for an adiabatic process

$$w = \frac{p_1 v_1}{\kappa - 1}\left\{1 - \left(\frac{v}{v}\right)^{\kappa-1}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Prob. 9. — Knowing that for air, $R = 29.27$ and $c_v = 0.169$, find c_p and prove that $\kappa = 1.405$. *Ans.* $c_p = 0.2375$.

Prob. 10. — Demonstrate that on a p-v diagram an adiabatic curve ($pv^{\kappa} = $ const.) at any given point is steeper than the isothermal ($pv = $ const.) passing through the same point.

Prob. 11. — Let the gas in Prob. 2 expand adiabatically, instead of at a constant pressure. What is the amount of heat converted into mechanical work? *Ans.* 81.12 kg-cal.

Prob. 12. — On a sheet of cross-section paper plot p-v curves of expansion, (a) at constant pressure, according to Prob. 2; (b) isothermal, Prob. 4; (c) adiabatic, Prob. 12. Mark on the curves the initial and the final temperatures, the work performed, and the heat supplied.

CHAPTER II.

WORK DONE BY EXPANDING A PERFECT GAS.

(b) Polytropic Changes.

BESIDES the fundamental cases of expanding a gas, considered in the preceding chapter, there are innumerable other combinations of simultaneous changes in pressure, volume, and temperature. The only condition which connects these three quantities is the characteristic equation of the gas

$$pv = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

so that two out of three of the quantities may be varied arbitrarily; the third is then determined from Eq. (1). As an example of such thermodynamic processes we shall consider in this chapter changes during which the quantity of heat supplied is proportional to the change in temperature (polytropic changes).

During a change of state at a constant volume the heat supplied to or withdrawn from the gas is proportional to the change in temperature, as is expressed by Eq. (2) in the preceding chapter. There are an infinite number of other processes in which the volume varies during the change and yet the quantity of heat supplied is proportional to the change in temperature. The problem is to find the general relation between p and v for such processes. The condition just stated leads to the equation

$$dh = c\,dT = c_v\,dt + A \cdot p\,dv, \quad . \quad . \quad . \quad (2)$$

which indicates that an increase in heat dh is proportional to the rise in temperature dT, and also that the heat supplied partly increases the intrinsic energy of the gas by the amount $c_v\,dT$, and is partly converted into external work $p \cdot dv$. The coefficient of proportionality c has the dimension of specific heat, and may be called the specific heat of a polytropic process, as distinguished from the specific heats c_p and c_v at constant pressure and at constant volume respectively.

Since the problem is to determine the relation between p and v, temperature T must be eliminated from Eq. (2) by means of the characteristic Eq. (1). By differentiating the latter we have:

$$R\,dT = p\,dv + v\,dp, \quad . \quad . \quad . \quad . \quad (3)$$

which, substituted into Eq. (2), gives

$$(c_v - c)\,(p\,dv + v\,dp) + ARp\,dv = 0.$$

But, according to Eq. (10) of the preceding chapter,

$$AR = c_p - c_v,$$

so that substituting and simplifying we find

$$\frac{dp}{p} + n\frac{dv}{v} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$n = \frac{c_p - c}{c_v - c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The integral of Eq. (4) is

$$\mathrm{Ln}\,(p_1/p_2) + n\,\mathrm{Ln}\,(v_1/v_2) = 0,$$

or

$$p_1v_1^n = p_2v_2^n = pv^n = \text{const.} \quad . \quad . \quad . \quad (6)$$

This is the required equation of a polytropic curve between p and v. (Note that the exponent n applies to v only, and *not* to the whole expression.) The general shape of such curves is shown in Fig. 7. When $n = 0$ (or $c = c_p$), $p = \text{const.}$, and the curve becomes a straight line parallel to the axis of abscissæ. For

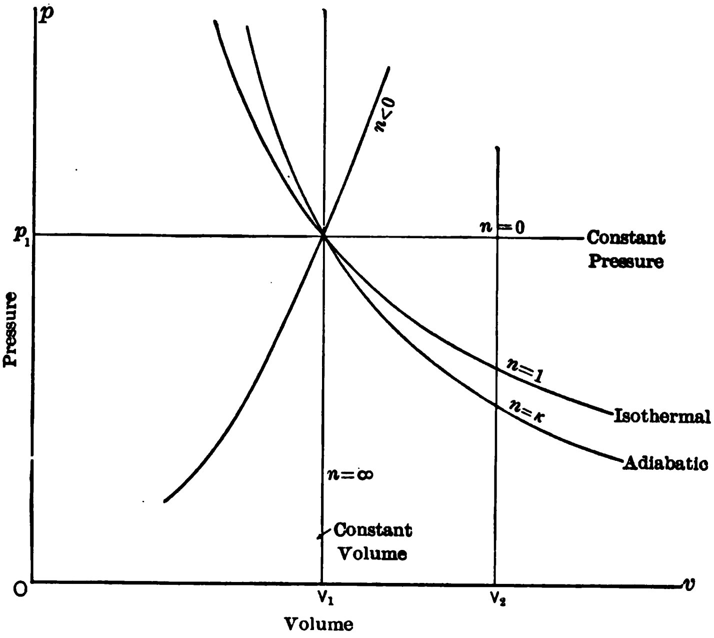

FIG. 7. — Polytropic changes in a perfect gas.

$n > 0$ the pressure decreases when the volume increases, and vice versa. For $n < 0$ both the volume and the pressure decrease and increase simultaneously. When $n = 1$, Eq. (6) becomes identical with Eq. (6) of the preceding chapter, and the change of state is isothermal. When $c = 0$

$$n = \frac{c_p}{c_v} = \kappa,$$

and the curve becomes an adiabatic; see Eq. (16) in the preceding chapter.

Prob. 1. — Plot a curve showing the relationship between c and n from $c = -\infty$ to $c = +\infty$. Explain the physical meaning of various values of c, and the corresponding shape of polytropic curves.

Prob. 2. — Prove that for a polytropic curve the ratio of an abscissa Or (Fig. 8) to the corresponding subtangent rg is constant and equal to the exponent n of the curve. This is one of the methods for determining this exponent when the curve is given as an experimental result.

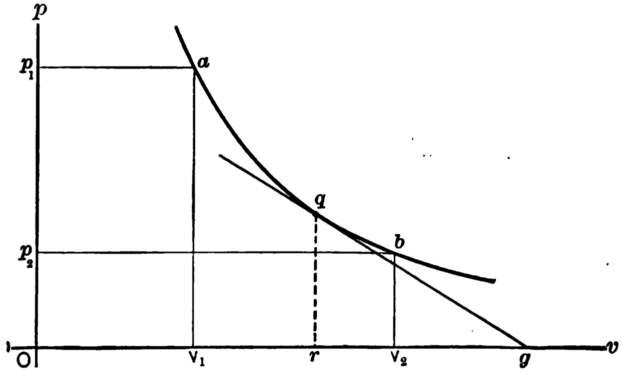

FIG. 8. — Determination of exponent n.

Prob. 3. — Find the relation between T and v by eliminating p from Eq. (2) and integrating the result. Show that the answer is the same as when p is eliminated directly between Eqs. (1) and (6).

Ans. $\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{n-1}$.

Prob. 4. — Find the relation between T and p by eliminating v from Eq. (2) and integrating the result. Show that the answer is the same as when v is eliminated between Eqs. (1) and (6).

Ans. $\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(n-1)/n}$.

Construction of Polytropic Curves.

It is sometimes required in the design of a gas engine, an air compressor, etc., to construct a polytropic curve according to Eq. (6), the exponent n and the initial pressure and volume being given. This can be done by assuming various values of p and calculating the corresponding v's with the acid of a table of logarithms, or it can be done graphically, using so-called logarithmic paper (Fig. 9). This is a cross-section paper on which divisions are proportional to logarithms of numbers, instead of being proportional to the numbers themselves.* When plotted on such paper all polytropic curves become straight lines of different slope. This becomes evident by taking logarithms of both sides of Eq. (6), viz.:

$$\log p + n \log v = \log p_1 + n \log v_1, \quad . \quad . \quad (7)$$

or denoting $\log v$ by x and $\log p$ by y

$$y + nx = \text{const.}$$

This is the familiar equation of a straight line, in which $(-n)$ is the tangent of the angle which the line makes with the x-axis.

An example will make the method clearer: Let air be compressed in the cylinder of an air compressor from atmospheric pressure and a temperature of 17° C. to a pressure of 6 metric atmospheres. If the compression were adiabatic the air would be heated considerably; to reduce the work of compression the air is cooled during the compression by spraying water into it. Assume that this makes the compression follow the law

$$pv^{1.2} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

instead of the adiabatic law

$$pv^{1.405} = \text{const.}$$

---

* If logarithmic cross-section paper is not available, the divisions on the upper scale of a slide rule may be used for the scale of coördinates.

It is required to construct the *p*-*v* curve according to Eq. (8).

From the characteristic equation we find at the atmospheric pressure ($p_1 = 1.0333 \times 10^4$ kg. per sq. m.),

$$v_1 = 29.27 \times (17 + 273)/10{,}333 = 0.8215 \text{ cu. m.}$$

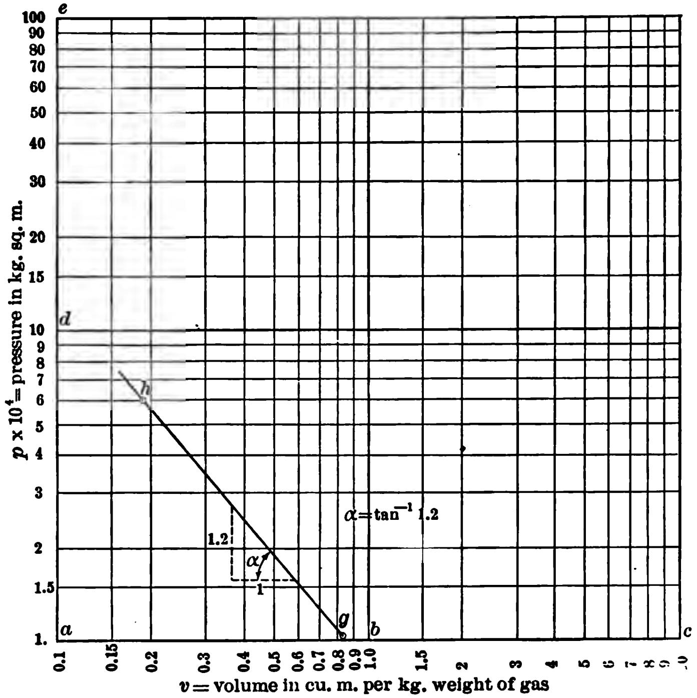

FIG. 9. — Use of logarithmic cross-section paper for plotting polytropic curves.

On the curve sheet (Fig. 9) the stretch *ab* corresponds to specific volumes from 0.1 to 1.0 cu. m. per kg. weight of gas, and the stretch *bc* to specific volumes from 1.0 to 10.0 cu. m. per kg. weight of gas. Along the axis of ordinates *ad* gives pressures from 10^4 to 10^5 kg. per sq. m., and *de* from 10^5 to 10^6 kg. per sq. m. The point

g is selected to correspond to $v_1 = 0.8215$ and $p_1 = 10{,}333$. Then the line gh is drawn at a slope of -1.2 to the axis of abscissæ. This line represents the required polytropic curve plotted to a logarithmic scale. It can either be used directly or re-plotted to an ordinary scale by simply transferring a sufficient number of points. At the pressure of 6 metric atmospheres (6×10^4 kg. per sq. m.), the specific volume, as determined from the curve, is $v_2 = 1.90$ cu. m. per kg. weight of gas (point h). The corresponding temperature is found from the characteristic equation:

$$T_2 = 1.90 \times 6 \times 10^4/29.27 = 389,$$

or

$$t_2 = 389 - 273 = 116^\circ \text{ C.}$$

The use of logarithmic paper enables one to judge whether or not a given curve of change of state is a polytropic curve, and if not, how near it comes to being one. This is done by transferring a sufficient number of points from the given curve (say, from an indicator card of a gas engine or an air compressor) to a logarithmic sheet. If all the points lie on a straight line the curve is of the form $pv^n = \text{const.}$, and the inclination of the straight line gives directly the value of n. Otherwise, it is possible to tell if n increases or decreases with the increase in volume, and also draw a straight line representing a polytropic curve which comes sufficiently close to the given curve.

If a curve is known to be polytropic and it is merely required to find n, we have, from Eq. (7),

$$n = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1}, \quad . \quad . \quad . \quad . \quad (9)$$

where the subscripts 1 and 2 refer to any two given points on the curve.

Prob. 5. — In the case shown in Fig. 9 what would be the final volume and temperature if the gas were allowed to be compressed adiabatically? Same isothermally? Transfer the three curves from logarithmic to ordinary cross-section paper in order to become familiar with the actual shape of the curves. Why is the work of compression greatest for the adiabatic curve and smallest for the isothermal curve?

Ans. Adiabatic, $t_2 = 209°$ C.; $v_2 = 0.235$ cu. m.;
Isothermal, $t_2 = 17°$ C.; $v_2 \doteq 0.1417$ cu. m.

Prob. 6. — Can the curve *gh* (Fig. 9) be drawn to a larger scale, using the same kind of logarithmic paper?

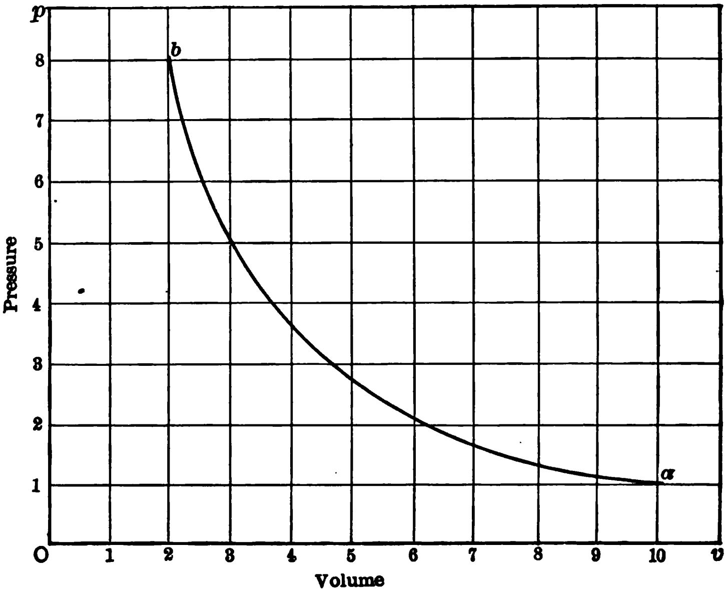

FIG. 10. — A change which is only approximately polytropic.

Prob. 7. — Determine if the curve *ab* shown in Fig. 10 is polytropic, and if not what is the equation of the nearest polytropic curve? What error would be made in determining *n* by directly using Eq. (9) between the two extreme points of the curve?

Work and Heat Values in Polytropic Changes.

Integrating Eq. (2) we get:

$$h = c\,(T_2 - T_1) = c_v\,(T_2 - T_1) + Aw,$$

where h is the total heat per unit weight of gas, supplied or abstracted between the states 1 and 2, and

$$w = \int_{v_1}^{v_2} p\,dv \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

is the external work done by the gas or upon the gas between the same states. We have thus

$$h = c\,(T_2 - T_1), \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

$$Aw = (c - c_v)\,(T_2 - T_1), \quad . \quad . \quad . \qquad (12)$$

or both the heat supplied and the work performed are proportional to the change in the temperature of the gas.

If it is desired to express h and w through pressures and volumes, instead of temperatures, Eqs. (1) and (6) may be used. Thus, combining Eqs. (1) and (12) gives

$$w = \frac{c - c_v}{AR}\,(p_2 v_2 - p_1 v_1),$$

or, remembering that $AR = c_p - c_v$,

$$w = \frac{c - c_v}{c_p - c_v}\,p_1 v_1 \left\{ \frac{p_2 v_2}{p_1 v_1} - 1 \right\}. \quad . \quad . \quad . \qquad (13)$$

In some cases in engineering practice the original pressure p_1 and volume v_1 are known, as well as the travel of the piston. Therefore the final volume v_2 is also known, while the final pressure p_2 is not immediately given. It is therefore desirable to eliminate it from the above equations by means of Eq. (6). Substituting, and taking Eq. (5) into account, the result is

$$w = \frac{p_1 v_1}{n - 1} \left\{ 1 - \left(\frac{v_1}{v_2}\right)^{n-1} \right\}. \quad . \quad . \quad . \qquad (14)$$

This formula is used to a considerable extent in thermodynamic calculations.

When gas is being compressed, instead of expanding, p_1 and v_1 in formula (14) represent the final, and not the initial, values (Fig. 8). If it is desired to use the initial values p_2 and v_2 in this case, formula (14) may be transformed by means of Eq. (6), which gives $p_1v_1 = p_2v_2\,(v_2/v_1)^{n-1}$. Substituting, we find

$$w = \frac{p_2v_2}{n-1}\left\{\left(\frac{v_2}{v_1}\right)^{n-1} - 1\right\}. \quad . \quad . \quad . \qquad (14a)$$

Prob. 8. — Derive formula (14) directly from Eqs. (10) and (6).

Prob. 9. — Prove that the ratio of the area p_1abp_2 (Fig. 8) to the area v_1abv_2 is equal to the exponent n of the polytropic curve. This gives a method for determining n by means of a planimeter. *Hint.* Area p_1abp_2 = area $v_1abv_2 + p_1v_1 - p_2v_2$.

Prob. 10. — When $n = 1$, expression (14) assumes an indeterminate form 0/0. Evaluate w in this case according to the general rule given in differential calculus for indeterminate expressions of this form. The result must check with Eq. (7) of the preceding chapter, since for $n = 1$ the change of state is isothermal.

Equation (14) in the Form of an Infinite Series.

Expression (14) is not convenient for numerical computations when the value of n is near unity. In this case, both the expression in the brackets and the denominator tend to become nearly zero, so that a small error in the values of v_1 and v_2 or of n may appreciably change the result. It is therefore convenient to expand the expression in the brackets into an infinite series of powers of $(n - 1)$. The value of $(n - 1)$ being small, the series converges rapidly, and a few terms usually suffice in practical calculations.

The expansion is performed according to the well-known Maclaurin series

$$f(x) = f(0) + \frac{x}{1} f'(0) + \frac{x^2}{2!} f''(0) + \frac{x^3}{3!} f'''(0) + \cdots .$$

In our case, denoting $(n - 1)$ by x, we have

$$f(x) = \left(\frac{v_1}{v_2}\right)^x ; f'(x) = \left(\frac{v_1}{v_2}\right)^x \operatorname{Ln}\frac{v_1}{v_2} ; f''(x) = \left(\frac{v_1}{v_2}\right)^x \left(\operatorname{Ln}\frac{v_1}{v_2}\right)^2 ; \text{ etc.}$$

$$f(0) = 1 ; f'(0) = \operatorname{Ln}\frac{v_1}{v_2} ; f''(0) = \left(\operatorname{Ln}\frac{v_1}{v_2}\right)^2 ; \text{ etc.,}$$

so that

$$1 - \left(\frac{v_1}{v_2}\right)^{n-1} = \frac{(n-1)}{1} \operatorname{Ln}\frac{v_2}{v_1} - \frac{(n-1)^2}{2!}\left(\operatorname{Ln}\frac{v_2}{v_1}\right)^2 + \cdots .$$

In this expression use is made of the transformation

$$\operatorname{Ln}\frac{v_1}{v_2} = -\operatorname{Ln}\frac{v_2}{v_1} ;$$

v_1 being, by assumption, smaller than v_2, Ln (v_1/v_2) is a negative quantity and may, therefore, for the sake of convenience, be replaced by a positive logarithm of the inverse ratio.

Thus, we finally have:

$$w = p_1 v_1 \operatorname{Ln}\frac{v_2}{v_1}\left\{1 - \frac{n-1}{2!}\left(\operatorname{Ln}\frac{v_2}{v_1}\right) + \frac{(n-1)^2}{3!}\left(\operatorname{Ln}\frac{v_2}{v_1}\right)^2 - \cdots\right\}. \tag{15}$$

This expression is preferable to Eq. (14) when n is near unity, because the terms in the brackets, from the second on, are small as compared to 1, and a slight error in their calculation is not liable to affect the result appreciably. When $n = 1$ Eq. (15) simply becomes

$$w = p_1 v_1 \, Ln \frac{v_2}{v_1}.$$

This is another way of evaluating the indeterminate form referred to in Prob. 10.

Prob. 11. — Calculate the expression w/p_1v_1, using both formulæ (14) and (15), in order to judge about their relative convenience and accuracy. Assume the ratio of expansion $v_2 : v_1$ to be equal to $4 : 1$, and $n = 1.05$.

Prob. 12. — It will be seen from Fig. 7 that the work done between the volumes v_1 and v_2 is smaller, the larger the exponent n, provided that the initial conditions are the same in all cases. Prove the same from formula (14); in other words, prove that with given values of p_1, v_1, and v_2 the value of w increases when n decreases.

Solution. — It is required to prove that

$$\frac{dw}{dn} < 0.$$

The given expression is equivalent to

$$y = \frac{1}{x}\left\{1 - \left(\frac{1}{r}\right)^x\right\},$$

where $x = n - 1$ and $r = \frac{v_2}{v_1} > 1$.

We have

$$\frac{dy}{dx} = \frac{-r^x + 1 + x\mathrm{Ln}r}{x^2r^x}.$$

The denominator is positive; to prove that the numerator is always negative let us find its maximum and minimum values. Thus, if

$$z = -r^x + 1 + x\mathrm{Ln}r,$$

$$\frac{dz}{dx} = \mathrm{Ln}r\,(1 - r^x) = 0;$$

in other words, the critical value of the function is for $x = 0$; at this value $z = 0$; the second derivative,

$$\frac{d^2z}{dx^2} = -(\mathrm{Ln}r)^2r^x,$$

is negative, hence the value $x = 0$ corresponds to a maximum of the function z. Thus, the maximum value of z is zero, hence z is always negative. This proves that

$$\frac{dy}{dx} < 0,$$

or that w decreases when n increases.

Work Expended in an Air Compressor.

A single-acting air compressor is represented schematically in Fig. 11. When the piston *P* is being moved upward, atmospheric air lifts the valve *s* and fills the cylinder. During the downward stroke, valve *s* is closed and the air is compressed during a part of the stroke to the desired pressure p_1, after which the valve *t* is opened and the compressed air is discharged into the storage tank *K* in which a constant pressure is maintained by means of the weighted piston *Q*. Then the same operations are repeated. The problem is to calculate the mechanical work done by the piston during one cycle comprising two strokes. Referring to Fig. 8, the net work performed per kilogram of air is represented by the area p_1abp_2. During the suction stroke, the atmospheric air performs the work Op_2bv_2;

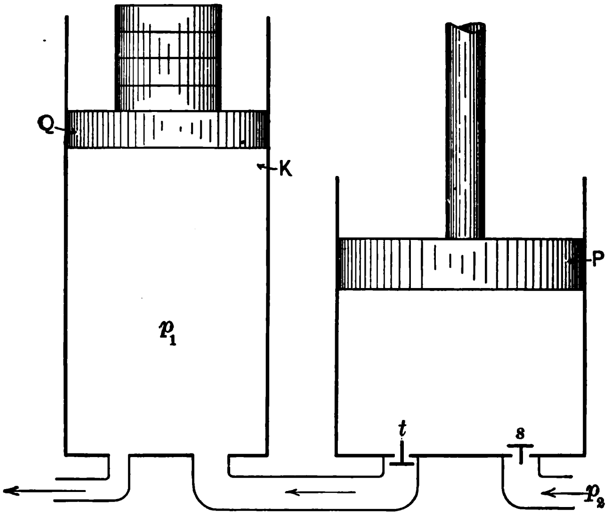

FIG. 11. — Schematic diagram of an air compressor.

during the compression period the piston performs the work represented by abv_2v_1, and finally during the discharge period the piston performs the work equivalent to Op_1av_1. Thus, the net work is

$$w = abv_2v_1 + Op_1av_1 - Op_2bv_2 = p_1abp_2. \quad . \quad (16)$$

The compression curve ab would be an adiabatic if the cylinder were impervious to heat; in reality the curve deviates considerably from an adiabatic, and for practical purposes it may be represented by a polytropic curve in which the exponent n varies for different compressors. Thus, using expression (14a) for the area abv_2v_1, Eq. (16) gives

$$w = \frac{p_2v_2}{n-1}\left\{\left(\frac{v_2}{v_1}\right)^{n-1} - 1\right\} + p_1v_1 - p_2v_2. \quad . \quad (17)$$

In this equation p_2 represents the atmospheric pressure, p_1 the pressure of the compressed air, v_2 the volume which one kilogram of air occupies at the atmospheric pressure p_2 and at a certain temperature T_2 which must be given. Volume v_1 corresponds to the pressure p_1 and to a certain temperature T_1 which may be calculated from Eqs. (1) and (6) if the exponent n is known.

Prob. 13. — Show that Eq. (17) may be simplified to

$$w = p_2v_2 \cdot \frac{n}{n-1}\left\{\left(\frac{v_2}{v_1}\right)^{n-1} - 1\right\}, \quad . \quad . \quad . \quad . \quad (18)$$

or to

$$w = p_2v_2 \cdot \frac{n}{n-1}\left\{\left(\frac{p_1}{p_2}\right)^{(n-1)/n} - 1\right\}. \quad . \quad . \quad . \quad (19)$$

Prob. 14. — Deduce Eq. (18) directly from Eq. (14a) on the basis of the theorem stated in Prob. 9.

Prob. 15. — A double-acting* compressor, working at a speed of 75 r.p.m., must deliver 1000 kg. of air per hour at a pressure of

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* This means that similar valves t and s (Fig. 11) are also placed on the top of the cylinder, so that air is compressed during both strokes. This doubles the work done with the same size of cylinder.

10 metric atmospheres (absolute). The air is taken at ordinary pressure and at room temperature (say, 20° C.). To determine: (*a*) the displacement of the cylinder; (*b*) kilowatts of the driving motor, assuming the efficiency of the compressor to be 75 per cent; (*c*) the temperature at which air is delivered; (*d*) per cent stroke at which the valve *t* must be opened. The exponent *n* may be assumed equal to 1.25.

Ans. (*a*) 0.0925 cu. m.; (*b*) 89.5 kw.; (*c*) 189° C.; (*d*) 83.73 %.

Compound Compressors.

Expression (19) shows that the work necessary for compressing one kilogram of air depends not only upon the initial and the final pressures, but also upon the final volume v_1 of the air. Now, with a given pressure, the volume depends on the temperature; therefore, in order to reduce the work of compression, the temperature during the compression must be kept as low as possible. This can be done by dividing the process of compression between two cylinders, and cooling the air on its way between the cylinders. Thus, referring to Fig. 11, the air is compressed in the first cylinder to a pressure p_m, intermediate between p_1 and p_2, and is delivered to the tank *K* where it is cooled as much as possible at a constant pressure, and then is delivered to a second compression cylinder where it is compressed to a higher pressure p_1. Such an arrangement is called a compound or a two-stage compressor.

The problem is to select the intermediate pressure p_m so as to reduce the total work of compression to a minimum.

Applying Eq. (19) we get

$$w=\frac{n}{n-1}\left\{p_2v_2\left[\left(\frac{p_m}{p_2}\right)^{(n-1)/n}-1\right]+p_mv_m\left[\left(\frac{p_1}{p_m}\right)^{(n-1)/n}-1\right]\right\} \quad (20)$$

or, introducing the corresponding temperatures T_2 and T_m which are known,

$$w = \frac{nR}{n-1}\left\{T_2\left[\left(\frac{p_m}{p_2}\right)^{(n-1)/n} - 1\right] + T_m\left[\left(\frac{p_1}{p_m}\right)^{(n-1)/n} - 1\right]\right\}. \quad (21)$$

The variable part of this expression, containing p_m, is

$$y = T_2\left(\frac{p_m}{p_2}\right)^{(n-1)/n} + T_m\left(\frac{p_1}{p_m}\right)^{(n-1)/n}, \quad . \quad . \quad (22)$$

and this must be a minimum if the work w is to be a minimum. The value of p_m which makes y a minimum may be found according to the general rule, by equating dy/dp_m to zero. However, it is much simpler to apply the theorem that when the product of two functions of a variable is constant, the sum of these functions is a minimum when the two functions are equal to each other (see Prob. 20 below). In our case

$$T_2\left(\frac{p_m}{p_2}\right)^{(n-1)/n} \cdot T_m\left(\frac{p_1}{p_m}\right)^{(n-1)/n} = T_2 T_m\left(\frac{p_1}{p_2}\right)^{(n-1)/n} = \text{const.};$$

hence the theorem holds true and the critical value of p_m is determined from the condition

$$T_2\left(\frac{p_m}{p_2}\right)^{(n-1)/n} = T_m\left(\frac{p_1}{p_m}\right)^{(n-1)/n},$$

whence

$$p_m = \sqrt{p_1 p_2} \cdot \left(\frac{T_m}{T_2}\right)^{\frac{1}{2}n/(n-1)} \quad . \quad . \quad . \quad . \quad (23)$$

If it is possible to cool the air to a temperature $T_m = T_2$ the preceding formula is simplified to

$$p_m = \sqrt{p_1 p_2}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Prob. 16. — Show from Eq. (21) that when p_m satisfies Eq. (23) the work done in the low-pressure cylinder is greater than that done in the high-pressure cylinder when $T_m > T_2$, and vice versa. What condition should p_m satisfy in order that equal amounts of work be done upon the gas in both cylinders?

Prob. 17. — Prove result (23) by directly differentiating Eq. (22).

Prob. 18. — Solve Prob. 15 assuming the machine to be a double-stage compressor, the air being cooled in the receiver to a temperature $T_m = 40°$ C.; determine the per cent saving in power.

Ans. $p_m = 3.79$ metric atmos. absolute;

(*a*)	Low-pressure cyl.	0.0925 cu. m.;	high-pressure,	0.0262 cu. m.
(*b*)	" "	46.43 kw.;	" "	35.52 kw.
(*c*)	. . . .			107° C.
(*d*)	" "	65.7 %	" "	54.0 %
			Per cent saving =	8.44.

Multi-stage Compressors.

When large quantities of air are to be compressed to very high pressures, and economy in operation is of importance, the work of compression is divided among three or more cylinders so that the air may be cooled in intermediate receivers. The problem is to determine the pressures in these receivers so that the total work of compression may be a minimum. By analogy with Eq. (22) we have

$$y = T_2\left(\frac{p_{m_1}}{p_2}\right)^{(n-1)/n} + T_{m_1}\left(\frac{p_{m_2}}{p_{m_1}}\right)^{(n-1)/n} \cdots + T_{mk}\left(\frac{p_1}{p_{mk}}\right)^{(n-1)/n} \qquad (25)$$

there being k intermediate receivers, or $k + 1$ compression cylinders; the pressures and the temperatures in these receivers are denoted by subscripts $m_1, m_2, \ldots,$ m_k. All the k intermediate pressures are independent variables; all the temperatures are supposed to be given. According to the general rule of differential calculus the k partial derivatives of y with respect to the k independent variables must be equated to zero; but here again advantage may be taken of the theorem proved in Prob. 21 below, since the product of all the terms constituting y is constant. Hence, all the terms must be equal to each other, or

$$T_2\left(\frac{p_{m_1}}{p_2}\right)^{(n-1)/n} = T_{m_1}\left(\frac{p_{m_2}}{p_{m_1}}\right)^{(n-1)/n} = \cdots = T_{mk}\left(\frac{p_1}{p_{mk}}\right)^{(n-1)/n}. \quad (26)$$

From these k equations the k unknown pressures may be easily determined.

Prob. 19. — Prove that when all the temperatures in Eq. (26) are equal, the pressure in each intermediate receiver is a geometric mean of the pressures in two adjacent receivers. In other words, the pressures increase according to a geometric progression whose ratio is

$$\left(\frac{p_1}{p_2}\right)^{1/k}.$$

Prob. 20. — To find a minimum value of the expression

$$y = u + v, \quad \dots \dots \dots \quad (27)$$

where both u and v are functions of the same independent variable x, and these functions are such that

$$uv = \text{const.} \quad \dots \dots \dots \quad (28)$$

Solution. The condition for a critical value of y is

$$dy = du + dv = 0,$$

while from Eq. (28)

$$u\,dv + v\,du = 0.$$

Eliminating du and dv from these two equations the result is

$$u = v. \quad \dots \dots \dots \quad (29)$$

It is left to the student to show that the values of u and v so found actually correspond to a minimum and not to any other critical value of y.

Prob. 21. — Referring to the preceding problem, let, in a more general case,

$$y = u_1 + u_2 + u_3 + \cdots + u_k, \quad \dots \quad (30)$$

where each of the u's is a function of n independent variables x_1, x_2, . . . , x_n. Let also the condition be fulfilled that the product

$$u_1u_2u_3 \dots u_k = C = \text{const.} \quad \dots \quad (31)$$

It is required to find the values of the u's for which y becomes a minimum. *Solution:* Function y has a critical value for the values of $x_1, x_2, \ldots, x_n$ determined from the equations

$$\frac{\partial y}{\partial x_1} = 0; \ \frac{\partial y}{\partial x_2} = 0; \ \frac{\partial y}{\partial x_3} = 0; \cdots \frac{\partial y}{\partial x_n} = 0.$$

In our case these conditions become

$$\left.\begin{array}{l} \dfrac{\partial u_1}{\partial x_1} + \dfrac{\partial u_2}{\partial x_1} + \dfrac{\partial u_3}{\partial x_1} + \cdots + \dfrac{\partial u_k}{\partial x_1} = 0, \\ \dfrac{\partial u_1}{\partial x_2} + \dfrac{\partial u_2}{\partial x_2} + \dfrac{\partial u_3}{\partial x_2} + \cdots + \dfrac{\partial u_k}{\partial x_2} = 0, \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \dfrac{\partial u_1}{\partial x_n} + \dfrac{\partial u_2}{\partial x_n} + \dfrac{\partial u_3}{\partial x_n} + \cdots + \dfrac{\partial u_k}{\partial x_n} = 0. \end{array}\right\} \quad . \ . \ . \ . \quad (32)$$

The condition (31) being differentiated in succession with respect to the various x's, gives

$$\left.\begin{array}{l} \dfrac{1}{u_1}\cdot\dfrac{\partial u_1}{\partial x_1} + \dfrac{1}{u_2}\cdot\dfrac{\partial u_2}{\partial x_1} + \cdots + \dfrac{1}{u_k}\cdot\dfrac{\partial u_k}{\partial x_1} = 0, \\ \dfrac{1}{u_1}\cdot\dfrac{\partial u_1}{\partial x_2} + \dfrac{1}{u_2}\cdot\dfrac{\partial u_2}{\partial x_2} + \cdots + \dfrac{1}{u_k}\cdot\dfrac{\partial u_k}{\partial x_2} = 0, \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \dfrac{1}{u_1}\cdot\dfrac{\partial u_1}{\partial x_n} + \dfrac{1}{u_2}\cdot\dfrac{\partial u_2}{\partial x_n} + \cdots + \dfrac{1}{u_k}\cdot\dfrac{\partial u_k}{\partial x_n} = 0. \end{array}\right\} \quad . \ . \ . \quad (33)$$

The two systems of equations must be satisfied simultaneously. This is possible only when

$$u_1 = u_2 = u_3 = \cdots = u_k = C^{1/k}. \quad . \ . \ . \ . \quad (34)$$

This is the required condition for min. y, although, strictly speaking, the values of y in the vicinity of the critical value must be investigated before one may state positively that condition (34) corresponds to a minimum and not to some other critical value of y; see Prob. 22.

To prove that Eq. (31) being differentiated with respect to x_1 gives the first Eq. (33): The partial derivative of Eq. (31) with respect to x_1 is

$$(u_2u_3 \dots u_k)\frac{\partial u_1}{\partial x_1} + (u_1u_3 \dots u_k)\frac{\partial u_2}{\partial x_1}$$
$$+ \dots + (u_1u_2 \dots u_{k-1})\frac{\partial u_k}{\partial x_1} = 0,$$

or

$$\frac{C}{u_1}\cdot\frac{\partial u_1}{\partial x_1} + \frac{C}{u_2}\cdot\frac{\partial u_2}{\partial x_1} + \dots + \frac{C}{u_k}\cdot\frac{\partial u_k}{\partial x_1} = 0.$$

Cancelling C the first equation (33) is obtained.

Prob. 22. — Prove that the values of u's according to Eq. (34) actually correspond to a minimum and not to a maximum of function y in Eq. (30). *Solution:* Solve Eq. (31) for u_k and substitute its value in Eq. (30). This gives

$$y = \sum_{1}^{k-1} u_i + C/(u_1u_2 \cdots u_{k-1}) \quad . \quad . \quad . \quad . \quad (35)$$

All the u's in this equation are independent of one another, so that for the critical value of y all the first partial derivatives of y must be separately equal to zero. Taking the derivative with respect to a variable u_i, we get

$$\frac{\partial y}{\partial u_i} = 1 - \frac{C}{u_1u_2 \cdots u_{k-1}}\cdot\frac{1}{u_i} = 0, \quad . \quad . \quad . \quad (36)$$

or

$$u_1u_2 \cdots u_{k-1}\cdot u_i = C. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Comparing this expression with Eq. (31) we see that

$$u_i = u_k. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Since the subscript i has all the values from 1 to $k - 1$, this result is identical with Eq. (34), and shows a simpler method of deriving it, by eliminating one of the variables.

Differentiating Eq. (36) again, we find two kinds of second partial derivatives:

$$\frac{\partial^2 y}{\partial u_i^2} = \frac{2C}{u_1u_2 \cdots u_{k-1}\cdot u_i^2} = \frac{2}{u_i} = \frac{2}{C^{1/k}} \quad . \quad . \quad . \quad (39)$$

and

$$\frac{\partial^2 y}{\partial u_i \partial u_j} = \frac{C}{u_1u_2 \cdots u_{k-1}\cdot u_iu_j} = \frac{1}{u_i} = \frac{1}{C^{1/k}} \quad . \quad . \quad (40)$$

Now let each variable receive some increment with respect to its critical value $C^{1/k}$, and let this increment for u_i be represented in the form ϵz_i, where ϵ is the same for all the u's, but z is different for each u. If we can prove that the difference between the new and the old value of y is positive for any small values of ϵz_i, then it will follow that y is a minimum for the critical values of the variables according to Eq. (34). Applying Taylor's series we have

$$\Delta y = \epsilon \sum_{1}^{k-1} z_i \frac{\partial y}{\partial u_i} + \tfrac{1}{2} \epsilon^2 \sum_{i=1}^{i=k-1} \sum_{j=1}^{j=k-1} z_i z_j \frac{\partial^2 y}{\partial u_i \partial u_j} + \text{etc.} \quad (41)$$

But at the critical point all the first derivatives according to Eq. (36) are equal to zero, and the values of the second derivatives are given in Eqs. (39) and (40). Consequently,

$$\Delta y = \tfrac{1}{2} \epsilon^2 [z_1^2 + z_2^2 + \cdots + z_{k-1}^2 + (z_1 + z_2 + \cdots + z_{k-1})^2]/C^{1/k} + \text{etc.} \quad . \quad . \quad . \quad (42)$$

The factor ϵ can now be taken so small that the term containing ϵ^2 is larger than all the succeeding terms put together. The expression in the brackets in Eq. (42) being a sum of squares is always positive; hence Δy is always positive whatever signs the z_i have. Therefore y is a minimum when the variables are all equal to each other, according to Eq. (34).*

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* The author is indebted to Dr. Virgil Snyder, professor of mathematics at Cornell University, for this proof.

CHAPTER III.

PRESSURE-TEMPERATURE CURVES OF SATURATED STEAM.

THE action of the steam engine and of the steam turbine is based upon the elastic properties of steam; therefore it is important for a research engineer to know how to represent these properties mathematically. One of the most important data on saturated steam is the relationship between its temperature and the pressure at which it is formed from liquid water. The underlying phenomenon is as follows (Fig. 12): Let a unit weight of water be contained in a cylinder *C*, covered with a piston. The piston is loaded with a weight *P* such as to produce upon the liquid a pressure of *p* kg. per sq. m. The water is gradually heated until steam begins to form under the piston. The temperature is then noted on the thermometer *T*. If more heat is added to the water, more steam is formed, and the piston begins to rise. By observing the thermometer it will be noted that the temperature now remains stationary until the last drop of water has been evaporated. After this, the temperature of the steam begins to rise, and it gradually acquires the

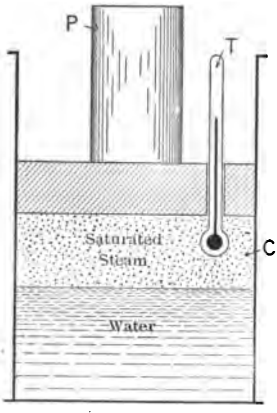

FIG. 12. — Saturated steam and water.

properties of a perfect gas considered in Chapters I and II. As long as liquid water is present the steam is called *saturated* and *its temperature depends only upon the pressure* p. Adding heat to it does not raise the temperature of the vapor, but merely increases the quantity of steam and decreases the amount of water.

So long as any water is present, steam is called *wet;* when the last drop of water has been evaporated the steam becomes *dry;* if more heat is added the steam becomes *superheated.*

The only way to obtain saturated steam at a higher temperature is to increase the pressure p. By repeating the same experiment with a larger weight P it will be found that the water must reach a higher temperature before steam begins to form. Thus, at ordinary atmospheric pressure, water begins to boil or steam is formed at 100° C. At a pressure of 5 (metric) atmospheres the temperature of water must reach about 151° C. before steam begins to be developed.

The experimental relationship between the pressure of saturated steam and the corresponding temperature is shown on the curve sheet Fig. 13. The true theoretical equation of this curve is unknown, although quite a number of empirical formulæ have been proposed which express this curve with a sufficient accuracy. For ordinary practical purposes no formulæ are required, values of pressures for different temperatures or vice versa being taken from numerous "steam tables," which represent corrected and interpolated experimental results. But there is one important property of saturated steam, namely, its density, which cannot be very accurately determined experimentally but which can be easily calculated from the shape of the p-t curve. Moreover, in some theoretical investigations involving

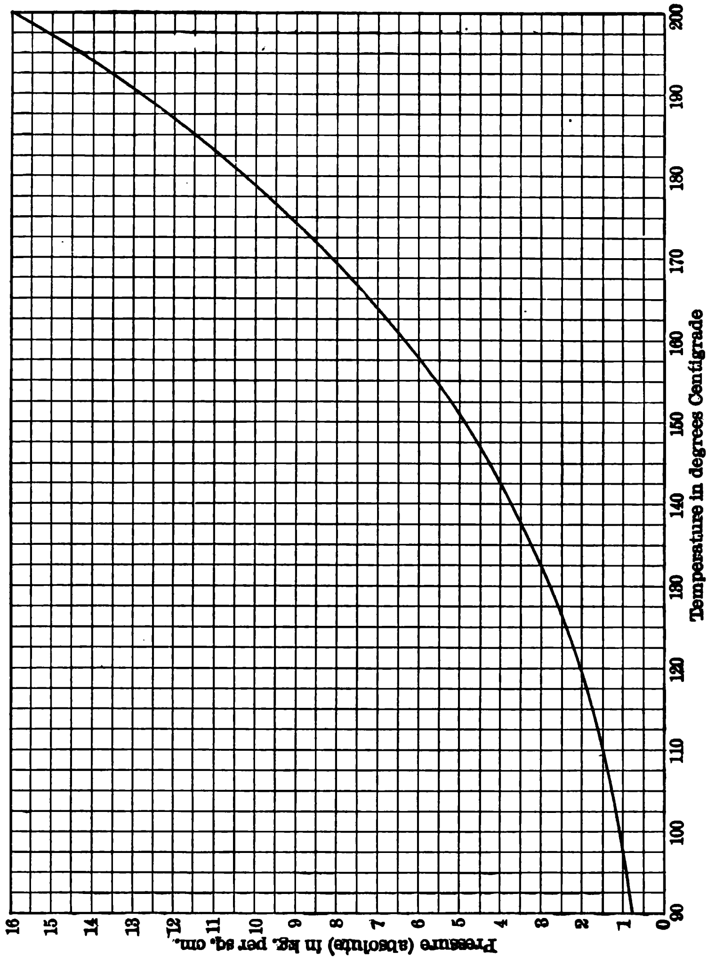

FIG. 13. — Experimental relationship between temperature and pressure of saturated steam.

differentiation and integration, it is necessary to have an analytical expression for the p-t curve of saturated steam.

Thus, the problem in this chapter is to investigate various analytical expressions for the curve given in Fig. 13 and to show methods for calculating the numerical coefficients entering into such formulæ. In doing so we shall limit ourselves to the range of temperatures between 100 and 200° C., as the most important in engineering work. The range between 40 and 100° C. is also of importance in condensing engines and low-pressure turbines, but the above range is sufficient in order to illustrate the mathematical method.*

In attempting to express a phenomenon by an empirical formula the simplest mathematical functions are tried first. Thus, there are two classes of functions or curves which have the general shape suggested by Fig. 13, namely parabolic curves of the form

$$p = Ax^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and exponential curves of the form

$$p = ae^{bt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The first curve would mean in our case that the pressure p increases as the nth power of the temperature; the second curve would indicate that the pressure increases in a geometric progression, when the temperature increases according to an arithmetic progression. Numerous empirical formulas have been proposed of the form (1) or (2), and some of them are considered below.

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* For an exhaustive treatment of the subject from the point of view of theoretical thermodynamics see G. A. Goodenough, "Thermal Properties of Steam," Bulletin No. 75 of the University of Illinois, 1914.

Parabolic Formulæ.

First assume the curve in Fig. 13 to be an ordinary parabola of the second degree with its vertex somewhere to the left of the curve sheet. Let the unknown pressure at the vertex be p_0 and the temperature t_0. With respect to this point as the origin, the ordinates increase as the squares of abscissæ, so that

$$(p - p_0) = A\,(t - t_0)^2, \quad . \quad . \quad . \quad . \quad (3)$$

where A is a coefficient of proportionality, to be determined from the given curve.

Eq. (3) contains three unknown quantities, t_0, p_0, and A. These may be determined by applying the equation to some three points on the given curve, for example, to the points corresponding to the temperatures of 100, 150 and 200° C. Denoting these temperatures t_1, t_2, and t_3, and the corresponding pressures by p_1, p_2, and p_3, and assuming that the theoretical curve (3) passes through these three points on the experimental curve, we have

$$p_1 - p_0 = A\,(t_1 - t_0)^2, \quad . \quad . \quad . \quad . \quad (4)$$

$$p_2 - p_0 = A\,(t_2 - t_0)^2, \quad . \quad . \quad . \quad . \quad (5)$$

$$p_3 - p_0 = A\,(t_3 - t_0)^2. \quad . \quad . \quad . \quad . \quad (6)$$

These three simultaneous equations may be solved with respect to p_0, t_0, and A. By subtracting Eq. (4) from Eq. (5), and Eq. (4) from Eq. (6) two new equations are obtained which do not contain p_0. Dividing one of these equations by the other the unknown quantity A is eliminated, and finally t_0 may be determined.

Expression (3) is of the first power with respect to p and of the second power with respect to t. It is therefore equivalent to the equation

$$p = a + bt + ct^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which the constants a, b, and c can be determined by writing Eq. (7) for some three points on the experimental curve (Fig. 13) and solving the three resulting simultaneous equations.

The actual shape of curve (3) or (7) depends on the three points selected on the given experimental curve. The best theoretical curve is not necessarily the one which crosses the experimental curve at the points corresponding to the temperatures of 100°, 150°, and 200° C. The best theoretical curve, or, as it is usually called, the most probable curve, may cross the experimental curve in some other points. Therefore, the above method does not give the best possible solution for the selected general form of Eq. (3) or (7). One way to improve the numerical coefficients is by inspection and trials; a more accurate procedure is to apply the *method of least squares* which is explained at the end of the chapter.

Prob. 1. — Obtain expressions for p_0, t_0, and A as explained above, plot curve (3), and determine the maximum per cent error or deviation from the experimental curve in Fig. 13.

Ans. With the data corresponding to $t = 100$, 150, and 200° C. the values are: $p_0 = 1.0263$ kg. per sq. cm.; $t_0 = 98.4°$ C.; $A = 0.001442$.

Prob. 2. — Express the constants a, b, and c through p_0, t_0, and A.

Ans. $a = (p_0 + At_0^2)$; $b = -2At_0$; $c = A$.

Prob 3. — Find the numerical values of the constants, a, b, and c, by solving the three equations which represent relationship (7) for some three points on the experimental curve.

Ans. For $t = 100$, 150, and 200° C., $a = 15$; $b = -0.2839$; $c = 0.001442$.

Prob. 4. — Solve the preceding problem in the general form, that is, find algebraic expressions for a, b, and c, when the parabola (7) is to pass through three given points on the experimental curve, these points being characterized by abscissæ t_1, t_2, and t_3, and ordinates p_1, p_2, and p_3.

The next parabolic formula to try is one of the form

$$p = At^n. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

This formula can be made to hold true only for a limited range of the curve, say between 100 and 200° C. It differs from Eq. (3) in that it represents a parabola of the nth degree, where n is to be determined from the experimental curve. Moreover, the constants p_0 and t_0 are at first assumed equal to 0 in order to make the formula simpler. Taking common logarithms we get

$$\log p = \log A + n \log t. \quad . \quad . \quad . \quad (7b)$$

Thus, plotted to a logarithmic scale for p and t, the curve becomes a straight line of the form $y = a + nx$. This fact suggests a simple method for determining A and n graphically: plot the given curve (Fig. 13) on a sheet of logarithmic paper and draw a straight line which comes nearest to the curve. The trigonometric tangent * of the angle which the curve makes with the axis of abscissæ gives the exponent n. Knowing n, the parameter A is determined from Eq. (7b) by substituting a pair of known values for p and t.

A parabolic formula which fits the experimental curve more closely is

$$p = A\,(t - t_0)^n. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It differs from Eq. (7a) in that it contains an additional constant t_0. The coefficient p_0 is again assumed equal to 0, in order to keep the number of constants down to three. A more rational and general formula would be

$$(p - p_0) = A\,(t - t_0)^n, \quad . \quad . \quad . \quad . \quad (9)$$

---

* The trigonometric tangent represents the actual slope of the line, and should be measured by an ordinary scale and not by the logarithmic scale.

which contains four coefficients and therefore can be made to pass through any four desired points on the given experimental curve. Applying Eq. (8) to some three given experimental sets of data we get:

$$\left.\begin{aligned} p_1 &= A\,(t_1 - t_0)^n, \\ p_2 &= A\,(t_2 - t_0)^n, \\ p_3 &= A\,(t_3 - t_0)^n. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From these equations A is easily eliminated by division, the result being

$$\left.\begin{aligned} \frac{p_3}{p_2} &= \left(\frac{t_3 - t_0}{t_2 - t_0}\right)^n, \\ \frac{p_2}{p_1} &= \left(\frac{t_2 - t_0}{t_1 - t_0}\right)^n. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From these two equations n may be eliminated by taking logarithms of both sides of the equations and dividing one result by the other. The resultant equation for t_0 is

$$\left.\frac{\log p_3 - \log p_2}{\log p_2 - \log p_1} = \frac{\log\left(\dfrac{t_3 - t_0}{t_2 - t_0}\right)}{\log\left(\dfrac{t_2 - t_0}{t_1 - t_0}\right)}\right\} \quad . \quad . \quad . \quad (12)$$

This equation can be solved by trial only, assuming different values for t_0, beginning, say, with zero. The procedure is not tedious, since the left-hand term of the equation is a known quantity. If in Eq. (12) the value of p_2 is so selected that

$$\frac{p_3}{p_2} = \frac{p_2}{p_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the left-hand side of the equation becomes equal to unity, and consequently

$$\frac{t_2 - t_0}{t_1 - t_0} = \frac{t_3 - t_0}{t_2 - t_0}. \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

From this equation t_0 may be found. Or the values of p_1, p_2, p_3 may be so selected that

$$\left(\frac{p_3}{p_2}\right)^{\frac{1}{2}} = \frac{p_2}{p_1}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

This makes the left-hand side of the equation equal to 2, so that a quadratic equation for t_0 is obtained.

Instead of eliminating n, the coefficient t_0 may be eliminated from Eq. (11), by extracting a root of the nth power and determining t_0 from both equations. The resultant equation for n must be solved by successive approximations unless the value of p_2 can be so selected as to satisfy Eq. (13) or (14), in which case n may be computed directly.

Eq. (8) plotted to a logarithmic scale gives a straight line

$$\log p = \log A + n \log (t - t_0),$$

between p and $(t - t_0)$. Therefore, in order to see how closely a parabolic curve checks with the given experimental curve, it is sometimes convenient to plot both curves on a sheet of logarithmic paper for comparison.

Prob. 5. — Plot the curve in Fig. 13 to a logarithmic scale and determine A and n in Eq. (7a). Check a few points with the original curve. *Ans.* $A = 0.127 \times 10^{-7}$; $n = 3.95$ (approx.).

Prob. 6. — Determine the numerical values of the coefficients in Eq. (8) first using Eqs. (12) and (13), then Eqs. (12) and (14).

Ans. For $p_1 = 1.03$ and $p_3 = 15.9$ kg. per sq. cm., by Eqs. (12) and (13), $t_0 = -48.6°$ C., by Eqs. (12) and (14), $t_0 = -39.1°$ C.

Prob. 7. — Determine the numerical values of the coefficients in Eq. (8) so that the curve would pass through the points corresponding to $t_1 = 100°$, $t_2 = 150°$, $t_3 = 200°$ C. *Hint.* — Solve for t_0 first by trial.

Ans. $t_0 = -39°$ C.; $n = 5.06$; $A = 0.149 \times 10^{-10}$.

Prob. 8. — Eliminate t_0 from Eqs. (11) and show how to determine n, A, and t_0. Also simplify the method for the case when either Eq. (13) or (14) is satisfied.

Prob. 9. — Outline the method by which the coefficients in formula (9) may be calculated. Determine roughly their numerical values, and check the results on a sheet of logarithmic paper.

If formula (7) does not represent experimental results with sufficient accuracy, it may be improved by adding further correction terms $dt^3 + et^4 + ft^5 + \cdots$. Or the terms added may be of the form

$$\frac{g}{t} + \frac{h}{t^2} + \cdots.$$

Trial alone can tell which form gives a better approach to the given curve. If it is desired to limit the number of terms to three, fractional exponents may be used, so that the formula becomes

$$p = a + bt^m + ct^n. \quad . \quad . \quad . \quad . \quad (15)$$

This formula contains five constants, and can therefore be made to pass through any five points on the given experimental curve. It can be made to fit it more closely than a curve with only three coefficients.

Another convenient formula with five coefficients is of the type

$$p = A\frac{(t+\alpha)^m}{(t+\beta)^n}. \quad . \quad . \quad . \quad . \quad (16)$$

It has the advantage over Eq. (15) in that the pressure p may be more conveniently calculated by means of a table of logarithms. For vapors of some substances satisfactory results are obtained by using only four instead of five constants in Eq. (16); that is, one may assume $\alpha = 0$, or $\beta = 0$, or $m = n$.

Prob. 10. — Show how to calculate the coefficients a, b, and m in formula (15), assuming $c = 0$.

Prob. 11. — Same as Prob. 10, only c is not equal to zero.

Prob. 12. — Show how to determine the coefficients in formula (16) when $m = n$. *Hint.*— Select on the experimental curve such points that $p_1 : p_2 = p_2 : p_3 = p_3 : p_4$, and denote $\sqrt[n]{p_4/p_3} = \sqrt[n]{p_3/p_2} = \sqrt[n]{p_2/p_1}$ by x; this quantity can then be eliminated. The problem is thus reduced to a solution of two simultaneous equations for α and β.

Logarithmic Formulæ.

We now turn our attention to the other class of formulæ of which the simplest is Eq. (2). Taking common logarithms the formula becomes

$$\log p = A + Bt, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where A and B are constant coefficients. If this formula expressed correctly the relationship between the pressure and the temperature of saturated steam, the experimental curve (Fig. 13) should become a straight line when plotted to a logarithmic scale for p and to a uniform scale for t. This is only approximately true, but may be accurate enough for some purposes.

Formula (17) may be improved by adding terms to it; for instance,

$$\log p = A + Bt + Ct^2 + \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Other self-evident modifications are

$$\log p = A + \frac{Bt}{C + t}; \quad . \quad . \quad . \quad . \quad (19)$$

$$\log p = A - \frac{B}{t} - \frac{C}{t^2}; \quad . \quad . \quad . \quad . \quad (20)$$

$$\log p = \alpha + \frac{\beta}{t} + \gamma \log t, \quad . \quad . \quad . \quad (21)$$

etc., etc.

Formula (19) was used to a considerable extent in the early days of steam engineering. Formula (20) is known as Rankine's formula. As a rule, absolute temperatures are used in it.

Prob. 13. — Replot the curve in Fig. 13, using a logarithmic scale for ordinates; draw a straight line that comes closest to the curve, and determine the constants A and B in formula (17).

Prob. 14. — Determine the numerical coefficients in formula (20), using absolute temperatures for t.

Ans. $A = 7.63$; $B = 3940$; $C = -423{,}600$ for
$T = 373°$ C., $423°$ C., and $473°$ C.

Formula of Biot and Regnault.

Regnault, to whom we are mainly indebted for our first knowledge of the properties of saturated steam, was confronted with the problem of presenting the relationship in Fig. 13 by a suitable formula. The simplicity of the formula was of secondary consideration, extreme accuracy being of prime importance. He selected the form known as Biot's formula

$$\log p = A + Bb^t + Cc^t, \quad . \quad . \quad . \quad (22)$$

which is somewhat similar to Eq. (18), except that the temperature enters as an exponent. Regnault probably found that this form of equation satisfied the results of his experiments better than any other forms known to him.* The curve corresponding to Eq. (22) may be made to pass through five points on the experimental curve, because the equation contains five coefficients; that is, Eq. (22) may be written for five known sets

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* The original form given by Regnault was

$$\log p = A + kb^{t-t_0} + lc^{t-t_0},$$

where t_0 is the lowest limit of the range of temperature to which the formula applies. Denoting kb^{-t_0} by B and lc^{-t_0} by C expression (22) is obtained.

of values of p and t, and the five simultaneous equations thus obtained may be solved for A, B, C, b, and c.

In the general case these five equations can be solved by trial only, which is an extremely tedious procedure. However, an exact solution is possible if the five pressures p are selected to correspond to equidistant temperatures; in other words, when

$$t_4 - t_3 = t_3 - t_2 = t_2 - t_1 = t_1 - t_0 = \delta. \quad . \quad (23)$$

The method for determining the constants in this case is as follows: Applying Eq. (22) to five equidistant points on the curve, we get

$$\left.\begin{aligned}\log p_0 &= A + Bb^{t_0} + Cc^{t_0},\\ \log p_1 &= A + Bb^{t_0+\delta} + Cc^{t_0+\delta},\\ \log p_2 &= A + Bb^{t_0+2\delta} + Cc^{t_0+2\delta},\\ \log p_3 &= A + Bb^{t_0+3\delta} + Cc^{t_0+3\delta},\\ \log p_4 &= A + Bb^{t_0+4\delta} + Cc^{t_0+4\delta}.\end{aligned}\right\} \quad . \quad . \quad . \quad (24)$$

These five simultaneous equations must be solved with respect to the five unknown coefficients A, B, b, C, c.

Subtract the first equation from the second, the second from the third, etc., in order to eliminate A. The result is

$$\begin{aligned}\log p_1 - \log p_0 &= Bb^{t_0}(b^\delta - 1) + Cc^{t_0}(c^\delta - 1),\\ \log p_2 - \log p_1 &= Bb^{t_0+\delta}(b^\delta - 1) + Cc^{t_0+\delta}(c^\delta - 1),\\ \log p_3 - \log p_2 &= Bb^{t_0+2\delta}(b^\delta - 1) + Cc^{t_0+2\delta}(c^\delta - 1),\\ \log p_4 - \log p_3 &= Bb^{t_0+3\delta}(b^\delta - 1) + Cc^{t_0+3\delta}(c^\delta - 1).\end{aligned}$$

Now denote

$$\left.\begin{aligned}Bb^{t_0}(b^\delta - 1) &= x,\\ Cc^{t_0}(c^\delta - 1) &= y,\\ b^\delta = v,\quad c^\delta &= w,\\ \log p_1 - \log p_0 &= q_0,\\ \log p_2 - \log p_1 &= q_1,\\ \log p_3 - \log p_2 &= q_2,\\ \log p_4 - \log p_3 &= q_3.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (25)$$

Then the four preceding equations assume the simple form

$$\left.\begin{aligned} q_0 &= x + y, \\ q_1 &= xv + yw, \\ q_2 &= xv^2 + yw^2, \\ q_3 &= xv^3 + yw^3. \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \qquad (26)$$

The standard method for solving such equations is to determine x from the first of them and to substitute its expression into the three remaining equations; then to determine y from one of the equations so obtained and to substitute its value into the remaining two. The result is two equations containing the unknown quantities v and w, which can easily be determined.

There is, however, a shorter way to eliminate x and y simultaneously, namely, the so-called method of indeterminate coefficients. Let us assume that one of the equations between v and w is the result of an elimination of x and y from the first three Eqs. (26), while the second equation between v and w is the result of the elimination of x and y from the last three Eqs. (26). Multiply the first Eq. (26) with an indeterminate coefficient P, the second with a similar coefficient Q, and add them to the third equation. The result is:

$$q_0P + q_1Q + q_2 = x\,(P + vQ + v^2) + y\,(P + wQ + w^2). \qquad (27)$$

This equation is true for any values whatever of P and Q. As our purpose is to eliminate x and y, we shall give P and Q such values that the coefficients of x and y shall become zero; in other words

$$\begin{aligned} P + vQ + v^2 &= 0, \\ P + wQ + w^2 &= 0, \end{aligned}$$

from which

$$\left.\begin{aligned} P &= vw, \\ Q &= -(v+w). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

Thus, Eq. (27) becomes

$$q_0 \cdot vw - q_1 (v+w) + q_2 = 0. \quad . \quad . \qquad (29)$$

It is not necessary to repeat this process for the last three Eqs. (26), because the equation obtained by their addition is identical with Eq. (27) except that xv stands for x and yw for y. Therefore, the values of P and Q are the same, and we can write directly

$$q_1 vw - q_2 (v+w) + q_3 = 0. \quad . \quad . \quad . \qquad (30)$$

Eqs. (29) and (30) can easily be solved for v and w. The simplest way is to consider vw to be one unknown quantity and $(v+w)$ to be the other. Using the notation of Eqs. (28) we have

$$\left.\begin{aligned} q_0 P + Q q_1 + q_2 &= 0, \\ q_1 P + Q q_2 + q_3 &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (31)$$

These must be solved for P and Q, and then Eqs. (28) solved for v and w. Knowing v and w, the unknown coefficients b, c, B, C are determined from Eqs. (25), and the problem is thus solved.

Prob. 15. — Show that by a direct elimination of x and y from Eqs. (26) results are obtained identical with (29) and (30).

Prob. 16. — Solve Eqs. (31) for P and Q.

Ans. $P = (q_3 q_1 - q_2^2)/(q_2 q_0 - q_1^2)$,
$Q = (q_2 q_1 - q_3 q_0)/(q_2 q_0 - q_1^2)$.

Prob. 17. — Solve Eqs. (28) for v and w.

Ans. $w = \frac{1}{2}(-Q \pm \sqrt{Q^2 - 4P})$; $v = \frac{1}{2}(-Q \mp \sqrt{Q^2 - 4P})$.

Prob. 18. — Determine the coefficients in formula (22) from five equidistant points on the curve in Fig. 13. Use five-place logarithms and be careful about the last significant figures.* *Note.* — δ must be odd in order to arrive at a real value for b or c.

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* Regnault used Vega's ten-place table of logarithms in the calculation of these coefficients.

Prob. 19. — Regnault found that at low temperatures and pressures the last term in Eq. (22) may be neglected. Show how to determine the coefficients A, B, and b in this case.

The Most Probable Curve.

With the method outlined above, the exact values of the coefficients in a formula depend upon the selection of the points on the experimental curve through which the approximate curve is supposed to pass. Thus, assuming, for instance, the form of the equation to be that represented by formula (7) the coefficients a, b, and c would probably be determined so that the curve would pass through the extreme and the middle points on the given curve (curve 2, Fig. 14). But this may not be the best solution. It is possible to modify

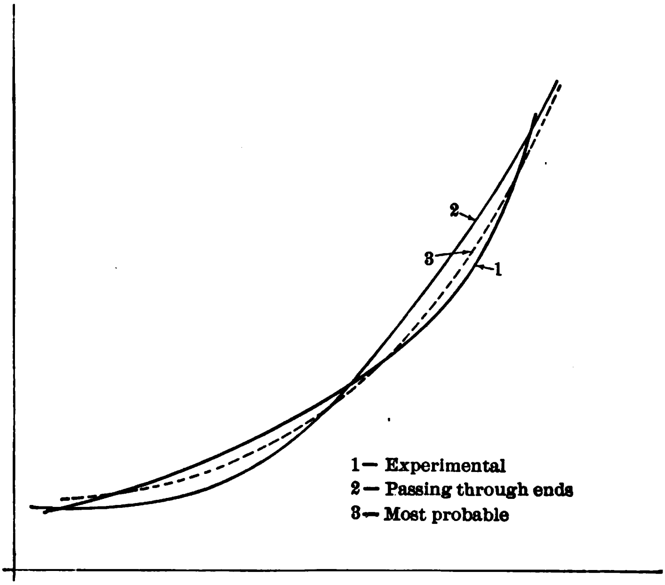

FIG. 14. — The most probable curve as distinguished from a curve which passes through the end points of the experimental curve.

slightly the coefficients a, b, and c in such a way as to make Eq. (7) check much more closely with the given curve (see dotted curve 3 in Fig. 14).

Upon first thought, the most probable curve seems to be the one for which the sum of the errors is a minimum. An " error " is here defined as the difference of the two ordinates corresponding to the same abscissa, one ordinate belonging to the experimental curve and the other to the assumed or calculated curve. But a closer reasoning will show that the sum of the errors for curve 2 (Fig. 14) may not be larger or may even be smaller than the sum of the errors for curve 3, because positive errors are balanced by negative errors. And yet it is evident that curve 3 satisfies the experimental results better than does curve 2.

It is shown in the theory of probabilities that for *the most probable curve the sum of the squares of the errors is a minimum.* One can readily see that whether an error is positive or negative its square is always positive; if the absolute values of errors are reduced by making the curve to pass more closely through the experimental points, the squares of the errors are reduced to a still greater degree. It is reasonable to assume that the curve for which the sum of the squares of the errors is a minimum is the best possible curve.

The above *law of least squares* is firmly established in application and one of the arguments in its favor is that in the simplest case of one quantity to be determined, the method leads to the arithmetical mean of the observations. For instance, let the distance between two fixed points be measured k times, in order to obtain a greater precision than is possible with a single measurement. Let the results be l_1, l_2, l_3, . . ., l_k, which differ slightly from one another. Let l be the most probable unknown value of the required distance. Then, if the law of the least squares is correct, the expression

$$\Sigma\,(\text{errors})^2 = (l - l_1)^2 + (l - l_2)^2 + \cdots + (l - l_k)^2$$

must be a minimum. Taking the first derivative of this expression with respect to the unknown quantity l, and equating it to zero, we have

$$2\,(l - l_1) + 2\,(l - l_2) + \cdots + 2\,(l - l_k) = 0,$$

or

$$l = \frac{l_1 + l_2 + \cdots l_k}{k}.$$

In other words the most probable value of the distance is the arithmetical mean of the observations, as is suggested by common sense. Perhaps this proof also gives an answer to the question as to why a sum of the squares is taken and not a sum of any other *even* powers of errors.

The simplest case of application of the method of least squares is found when the dependent variable, in our case p, and the coefficients to be determined, such as a, b, and c, in Eq. (7), enter in a linear form. Take any number of points on the experimental curve, say, twenty or thirty, and let them be determined by the abscissæ $t_1, t_2, \ldots, t_k$, and by the ordinates $p_1, p_2, \ldots, p_k$. The theoretical curve (7), as a rule, does not pass through any of these points, so that Eq. (7) becomes

$$\left.\begin{aligned} p_1 + \Delta_1 &= a + bt_1 + ct_1^2, \\ p_2 + \Delta_2 &= a + bt_2 + ct_2^2, \\ &\cdots\cdots\cdots, \\ &\cdots\cdots\cdots, \\ p_k + \Delta_k &= a + bt_k + ct_k^2, \end{aligned}\right\} \quad \ldots \quad (32)$$

where $\Delta_1, \Delta_2, \ldots, \Delta_k$ are small errors between the values of p calculated from Eq. (7) and those actually observed.

According to the law of least squares, if the coefficients in Eq. (7) have been properly selected so as to give the most probable curve, the errors satisfy the condition

$$\Delta_1^2 + \Delta_2^2 + \cdots + \Delta_k^2 = \text{min.},$$

or

$$\sum_{i=1}^{i=k}(a + bt_i + ct_i^2 - p_i)^2 = \text{min.} \quad . \quad . \quad . \quad (33)$$

In this equation all the p's and t's are taken from the experimental curve. The only unknown variable quantities are the coefficients a, b, and c. Since these coefficients are independent of each other, function (33) becomes a minimum when each of the three partial derivatives

$$\frac{\partial\Sigma}{\partial a}, \quad \frac{\partial\Sigma}{\partial b}, \quad \frac{\partial\Sigma}{\partial c}$$

is separately equal to zero.

Performing the differentiation and dividing by 2, we get

$$\left.\begin{aligned} \Sigma\ (a + bt + ct^2 - p) &= 0, \\ \Sigma t\ (a + bt + ct^2 - p) &= 0, \\ \Sigma t^2 (a + bt + ct^2 - p) &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad (34)$$

where the subscripts i are omitted for the sake of brevity. Simplifying, we obtain:

$$\left.\begin{aligned} ka + b\Sigma t + c\Sigma t^2 &= \Sigma p, \\ a\Sigma t + b\Sigma t^2 + c\Sigma t^3 &= \Sigma pt, \\ a\Sigma t^2 + b\Sigma t^3 + c\Sigma t^4 &= \Sigma pt^2. \end{aligned}\right\} \quad . \quad . \quad . \quad (35)$$

Solving these simultaneous equations for a, b, and c, the most probable curve is obtained. It will be observed that when using the method of least squares it is not necessary to specify in advance through which points the curve should pass, nor are we limited in the number of experimental points to be used in the solution of Eqs. (35).

Prob. 20. — Determine the coefficients A and B in Prob. 13, by the method of least squares, and see how close the curve thus determined comes to the one drawn according to the judgment of the eye.

Ans. For the ten points, $t = 100, 110, 120, \ldots, 190°$ C.,
$A = -1.174$, $B = 0.1224$.

A Method for Improving Empirical Formulæ.

A weak point in the above-described application of the method of least squares is that the coefficients which enter into equations such as Eq. (35) are usually large numbers. Thus, in our case t varies between 100 and 200, so that t^4 is of an order of magnitude of thousands of millions. Dealing with such large numbers is not only inconvenient, but may cause inaccuracy in multiplication and division. Thus, an error of one per cent in any of the Σ's introduces a corresponding error in the magnitudes of a, b, and c. At the same time, unless a, b, and c can be determined with considerable accuracy, the whole method of least squares is superfluous, since approximate values of coefficients can be determined by simple trials. Therefore, it is preferable first to calculate some approximate values of the coefficients in question without the use of the method of least squares, and then to apply the method of least squares to *finding corrections* to these approximate values which will make them more accurate. This procedure is technically known as "improving" empirical formulæ. An example will make it clearer.

Let the best numerical value of a coefficient in an empirical formula be 28.45(7), the digit in the parentheses being uncertain. If this value be calculated by the method of least squares, from equations such as (34), computations must be conducted with an accuracy of at least six significant figures, the last one or two being lost during the transformations. Let, however, the approximate value of the same coefficient, say, 28.1, be determined by some other method, for instance, by assigning three points through which the theoretical curve is supposed to pass. Then the method of least squares need be applied only to the correction 0.35(7) of this value (in the manner indicated below); it is sufficient to compute with, say, only four significant figures. Moreover, with such a procedure, some of the coefficients in Eq. (35) assume much more convenient values and are easier to handle.

Let A, B, and C be some known approximate values of a, b, and c, and let α, β, and γ be small unknown corrections of these values, so that

$$\left.\begin{aligned} a &= A + \alpha, \\ b &= B + \beta, \\ c &= C + \gamma. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Substitute these expressions in the first Eq. (32); the result is

$$p_1 + \Delta_1 = A + \alpha + Bt_1 + \beta t_1 + Ct_1^2 + \gamma t_1^2,$$

or

$$r_1 + \Delta_1 = \alpha + \beta t_1 + \gamma t_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where

$$r_1 = p_1 - (A + Bt_1 + Ct_1^2). \quad . \quad . \quad . \quad (38)$$

Here r_1 is a small quantity, being the difference between the observed p_1 and that calculated from the approximate formula

$$p = A + Bt + Ct^2.$$

Thus, Eq. (37) is identical in form with Eq. (32), except that small quantities r, α, β, and γ enter in place of large quantities p, a, b, and c. By identical reasoning with that given above, we arrive at the conclusion that the corrections α, β, and γ must satisfy equations identical in form with Eqs. (35), namely

$$\left.\begin{aligned} k\alpha + \beta\Sigma t + \gamma\Sigma t^2 &= \Sigma r, \\ \alpha\Sigma t + \beta\Sigma t^2 + \gamma\Sigma t^3 &= \Sigma rt, \\ \alpha\Sigma t^2 + \beta\Sigma t^3 + \gamma\Sigma t^4 &= \Sigma rt^2. \end{aligned}\right\} \quad . \quad . \quad . \quad (39)$$

Solving these for α, β, and γ, and substituting the values into Eqs. (36), the most probable values of a, b, and c are obtained.

Prob. 21. — Determine approximate values of a, b, and c in Eq. (7) so that the curve will pass through the points corresponding to $t = 100, 150$, and 200° C. Then calculate corrections according to the method of least squares [use Eqs. (39)], selecting from ten to fifteen equidistant points on the curve. Plot the most probable curve on the same sheet with the experimental curve and with the curve of first approximation.

Ans. $\alpha = 19.4$; $\beta = -0.267$; $\gamma = 0.00085$; New equation therefore reads $p = 34.4 - 0.551\,t + 0.00229\,t^2$.

Non-linear Equations.

The method outlined above cannot be used directly when the given equation is not linear with respect to the unknown coefficients. Take, for instance, Eq. (7a): proceeding as in Eq. (32) we get

$$\left.\begin{aligned} p_1 + \Delta_1 &= At_1^n, \\ p_2 + \Delta_2 &= At_2^n, \\ . \quad . \quad . \quad &. \quad . \quad . \ , \\ . \quad . \quad . \quad &. \quad . \quad . \ , \\ p_k + \Delta_k &= At_k^n. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

According to the law of least squares the most probable values of A and n satisfy the equation

$$\Sigma\,(At^n - p)^2 = \text{min.}$$

The partial derivative of this expression with respect to A being equated to zero gives

$$\Sigma t^n\,(At^n - p) = 0.$$

The partial derivative with respect to n gives

$$\Sigma At^n \mathrm{Ln}t\,(At^n - p) = 0,$$

or, after reduction,

$$\left.\begin{aligned} A\Sigma t^{2n} - \Sigma pt^n &= 0, \\ A\Sigma t^2\mathrm{Ln}t - \Sigma pt^n\mathrm{Ln}t &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad (41)$$

The unknown quantities A and n enter into these equations in such a form that it is impossible to solve the equations. Such a case invariably arises when the coefficients do not appear in the given equation, such as Eq. (7a), in the linear form. The following artifice is used in this case in order to obtain linear equations in place of Eqs. (41). The coefficients A and n are again determined first approximately, for instance, as in Prob. 5. Let A' and n' be the approximate values, so that the most probable values are

$$\left.\begin{aligned} A &= A' + \alpha, \\ n &= n' + \nu, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where α and ν are small quantities. Let the equation of the approximate curve be

$$p' = A't^{n'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

while the equation of the most probable curve is

$$p = At^n = (A' + \alpha)\,t^{n'+\nu} \quad . \quad . \quad . \quad (43a)$$

According to Taylor's theorem for two variables we have

$$p = p' + \frac{\alpha}{1} \cdot \frac{\partial p'}{\partial A'} + \frac{\nu}{1} \cdot \frac{\partial p'}{\partial n'} + \frac{\alpha^2}{1 \cdot 2} \frac{\partial^2 p'}{\partial A'^2} + \cdot \cdot \cdot \cdot \quad (44)$$

But, according to our supposition α and ν are small quantities; therefore all the terms of the series, with the exception of the first three, may be neglected. Substituting the values of p' and its derivatives from Eq. (43) we have *approximately*

$$At^n = A't^{n'} + \alpha t^{n'} + \nu A't^{n'}\text{Ln}t.$$

Hence, the first of the Eqs. (40) becomes

$$p_1 + \Delta_1 = A't_1^{n'} + \alpha t_1^{n'} + \nu \cdot A't_1^{n'}\text{Ln}t_1, \quad . \quad (45)$$

or, introducing

$$r_1 = p_1 - A't_1^{n'},$$

we obtain

$$\left.\begin{aligned} \Delta_1 &= \alpha t_1^{n'} + \nu A't_1^{n'}\text{Ln}t_1 - r_1, \\ \Delta_2 &= \alpha t_2^{n'} + \nu A't_2^{n'}\text{Ln}t_2 - r_2, \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad , \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad , \\ \Delta_k &= \alpha t_k^{n'} + \nu A't_k^{n'}\text{Ln}t_k - r_k. \end{aligned}\right\} \quad . \quad . \quad . \quad (46)$$

These are linear equations with respect to the unknown corrections α and ν. Therefore, applying the condition $\Sigma\Delta^2 = \text{min.}$, and taking partial derivatives with respect to α and ν, we obtain two linear equations from which α and ν are easily calculated.

To the beginner this method may seem somewhat circuitous, but it is based upon the simple theorem that when the coefficients in a function receive *small* increments, the increase in the function itself is a linear function of these increments. In our case we change from the known function p', Eq. (43), to the unknown function p, by giving the coefficients A' and

n' unknown increments α and ν; Eq. (44) indicates that the difference $p - p'$ is a linear function of these increments. The difficulty with Eqs. (40) is that the right-hand side is not a linear function of the unknown coefficients A and n. By the above artifice it is reduced to the form (45) in which the right-hand side consists of a known function $A't_1^{n'}$ which need not be linear, and of a linear expression containing the unknown corrections α and ν.

Prob. 22. — From Eqs. (46) obtain two expressions for α and ν, which take the place of Eqs. (41).

Ans. (1) $\alpha\Sigma t^{2n'} + A'\nu\Sigma t^{2n'}\mathrm{Ln}t = \Sigma rt^{n'}$;

(2) $\alpha\Sigma t^{2n'}\mathrm{Ln}t + A'\nu\Sigma t^{2n'}(\mathrm{Ln}t)^2 = \Sigma rt^{n'}\mathrm{Ln}t$.

Prob. 23. — Using the results of Prob. 5 as the first approximation, determine more accurate values of A and n by the method of least squares. *Hint.* — Use 4-place tables of logarithms for computing r, and be careful of the last figure. After obtaining two simultaneous equations for α and ν, use long-hand calculation for all changes, as the two equations differ very little from each other, the first difference appearing in the fourth figure.

Ans. $\alpha = 0.011 \times 10^{-7}$; $\nu = -0.018$.

New equation reads $p = 0.1383 \times 10^{-7}\, t^{3.932}$.

Prob. 24. — Show how to improve the coefficients in Rankine's formula (20) by the method of least squares. *Solution.* — The usual way would be to represent the formula in the form

$$p' = 10^{A' - \frac{B'}{t} - \frac{C'}{t^2}}.$$

and to expand it according to Eq. (44). After this has been done formulæ are obtained corresponding to Eqs. (45) and (46). The student is advised to follow this method and to obtain final expressions for the corrections α, β, and γ, in order that he may be sure that he understands the general method. The same results can, however, be obtained in a somewhat simpler way by the following artifice:

$$\begin{aligned}\log p &= \log\,[p' + (p - p')] = \log p'\left(1 + \frac{p - p'}{p'}\right)\\ &= \log p' + M\left[\frac{p - p'}{p'} - \frac{1}{2}\left(\frac{p - p'}{p'}\right)^2 + \cdots\right],\end{aligned}$$

where $M = \log e = 0.43429$ is the modulus of common logarithms, and the expression in the last brackets represents the expansion of a logarithmic function into an infinite series. The difference between the accurate value p and the approximate value p' is small, so that all the terms of the series may be neglected, except the first. Solving for $p - p'$ gives

$$p - p' = \frac{p'}{M}(\log p - \log p'),$$

or taking into account expression (20),

$$p - p' = \frac{p'}{M}\left(\alpha - \frac{\beta}{t} - \frac{\gamma}{t^2}\right).$$

Hence, the expressions corresponding to Eqs. (40) become

$$\left.\begin{array}{l} p_1 + \Delta_1 = p_1' + \dfrac{p_1'}{M}\alpha - \dfrac{p_1'}{Mt_1}\beta - \dfrac{p_1'}{Mt_1^2}\gamma, \\ p_2 + \Delta_2 = p_2' + \dfrac{p_2'}{M}\alpha - \dfrac{p_2'}{Mt_2}\beta - \dfrac{p_2'}{Mt_2^2}\gamma, \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ , \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ , \\ p_k + \Delta_k = p_k' + \dfrac{p_k'}{M}\alpha - \dfrac{p_k'}{Mt_k}\beta - \dfrac{p_k'}{Mt_k^2}\gamma. \end{array}\right\} \quad . \ . \ . \quad (47)$$

These expressions are linear with respect to the unknown corrections α, β, and γ. Denoting as before the difference $p_1 - p'$ by r_1, the law of the least squares gives:

$$\sum\left(p'\alpha - \frac{p'\beta}{t} - \frac{p'\gamma}{t^2} - Mr\right)^2 = \text{min.},$$

or, taking partial derivatives,

$$\sum p'\left(p'\alpha - \frac{p'\beta}{t} - \frac{p'\gamma}{t^2} - Mr\right) = 0,$$

$$\sum \frac{p'}{t}\left(p'\alpha - \frac{p'\beta}{t} - \frac{p'\gamma}{t^2} - Mr\right) = 0,$$

$$\sum \frac{p'}{t^2}\left(p'\alpha - \frac{p'\beta}{t} - \frac{p'\gamma}{t^2} - Mr\right) = 0.$$

After simplification we get

$$\left.\begin{array}{l} \alpha\sum p'^2 - \beta\sum\dfrac{p'^2}{t} - \gamma\sum\dfrac{p'^2}{t^2} - M\sum rp' = 0, \\ \alpha\sum\dfrac{p'^2}{t} - \beta\sum\dfrac{p'^2}{t^2} - \gamma\sum\dfrac{p'^2}{t^3} - M\sum\dfrac{rp'}{t} = 0, \\ \alpha\sum\dfrac{p'^2}{t^2} - \beta\sum\dfrac{p'^2}{t^3} - \gamma\sum\dfrac{p'^2}{t^4} - M\sum\dfrac{rp'}{t^2} = 0. \end{array}\right\} \quad . \ . \quad (48)$$

From these three equations the corrections α, β and γ may be calculated.

Prob. 25. — Eqs. (48), from which the corrections are to be calculated, are obtained in a definite manner from Eqs. (47). These latter equations are also linear with respect to the corrections α, β, γ, etc., of the general form

$$\begin{aligned}\Delta_1 &= \alpha X_1 + \beta Y_1 + \gamma Z_1 + \cdots - R_1,\\ \Delta_2 &= \alpha X_2 + \beta Y_2 + \gamma Z_2 + \cdots - R_2,\\ &\ldots\ldots\ldots\ldots\ldots\ldots,\\ &\ldots\ldots\ldots\ldots\ldots\ldots,\\ \Delta_k &= \alpha X_k + \beta Y_k + \gamma Z_k + \cdots - R_k.\end{aligned}$$

Deduce the rule according to which the coefficients in Eqs. (48) are formed from $X, Y, Z, \ldots, R$. With such a rule there may be no need of actually differentiating every time, in practical applications, but equations such as (48) may be written down as soon as the problem is reduced to the linear form of Eq. (47).

CHAPTER IV.

HEAT OF VAPORIZATION AND DENSITY OF SATURATED STEAM.

THE phenomenon of vaporization of water under pressure, described at the beginning of the previous chapter, involves two quantities which are of prime importance in the design of steam engines and turbines, namely, heat of vaporization and specific weight or density of steam. Let us assume that at the beginning of the experiment there is no steam in the vessel, and that the water is brought up to the temperature at which steam just begins to be formed (this temperature depends upon the pressure exerted upon the piston, see Fig. 13). As soon as vaporization begins, the temperature remains constant until the last drop of water has been converted into steam. Hence, all the heat communicated to the mixture of water and steam is used for two purposes:

(*a*) to raise the weight of the piston (external work);

(*b*) to separate particles of the water in converting it into steam (internal work).

Experiment shows that at usual pressures and temperatures the internal work is several times as great as the external.

It will be remembered that in a perfect gas the disgregation work is zero, so that in an isothermal process, as is the one under consideration, all the heat received is converted into external work. In the case of a saturated vapor, however, many times more heat must be communicated than the amount converted into work. This heat remains in steam in a " latent state," and is liberated again when the steam is condensed into water. Thus,

Total heat of vaporization = A (external work)
+ (internal latent heat),

where A is the coefficient for the conversion of work units into heat units (see p. 9). The external work can be easily calculated since the expansion is performed at a constant pressure.

$$\text{External work} = \int_{v_1}^{v_2} p\,dv = p\,(v_2 - v_1),$$

where v_1 is the specific volume of water, v_2 is that of steam. It is customary to denote $(v_2 - v_1)$ by u, or

$$u = v_2 - v_1,$$

where u stands for the increase in the specific volume of saturated steam over that of water. For instance, at 150° C. one kilogram of saturated steam occupies a volume $v_2 = 0.3876$ cu. m., while one kilogram of water at the same temperature occupies less than 0.001 cu. m. Thus, at 150° C. $u = 0.3876 - 0.001$ or 0.3866 cu. m. per kg. It will be seen from this example that for most practical purposes v_1 may be neglected and u considered equal to v_2. The above equation then becomes

$$r = Apu + \rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the total heat of vaporization, ρ is the internal heat of vaporization, and the difference of the two, Apu, represents the external work done; r, ρ, and u are, of course, values for unit weight of working substance.

Prob. 1. — At a temperature of 150° C., steam has a pressure of 4.869 kg. per sq. cm., and $r = 500.79$ kg-cal. What per cent of total heat r is converted into work, and how much is retained by the steam as internal latent heat ρ? *Hint.* v_1 and v_2 are given above. *Ans.* 8.81 per cent; 91.19 per cent.

Relation between *r* and *u*.

Total heat of vaporization r, and specific volume u, can be determined separately by experiment. There is, however, a general theoretical relation between the two, so that when one of them is known the other may be calculated. This relation, known as Clapeyron's equation, may be deduced as follows: Let a unit weight of water perform a thermal cycle indicated in Fig. 15. At A the water is all liquid; it occupies a certain volume v_1, has a pressure p, and a temperature T (absolute) such that the water is about to vaporize. Heat is now being added to the water, which vaporizes until at B we have dry saturated steam. Dur-

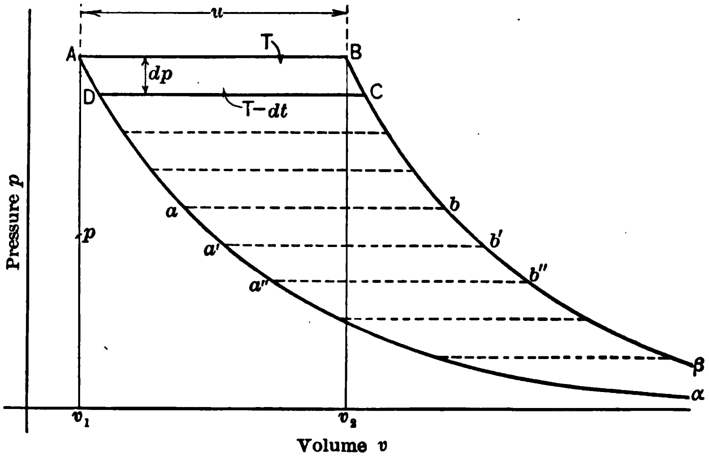

Fig. 15. — A thermodynamic cycle performed by a mixture of water and steam.

ing this process both the pressure and temperature remain constant. At B the pressure is relieved by an infinitesimal amount dp, and the steam allowed to expand *adiabatically* (see p. 15) along the line BC, its temperature dropping by dT. After this, the two processes are repeated in the reverse order; that is, first, heat is withdrawn at the temperature $T - dT$, so that the steam condenses into water along the isothermal CD, and secondly, the pressure is again increased by the amount dp, so that the substance is returned to its original condition along the adiabatic DA. Since the substance has now the same heat content as at the beginning of the cycle, the net amount of heat expended during the process is equal to the mechanical work performed during the cycle. The mechanical work is expressed on the diagram by the area $ABCD$, or is equal to

$$(v_2 - v_1)\,dp = u\,dp. \quad . \quad . \quad . \quad . \quad (2)$$

The total heat communicated to the mixture during the isothermal expansion AB is equal to the heat of vaporization r. Of this only a small part is converted into work, the rest, r', being rejected at the temperature $T - dT$ during the isothermal compression CD. Heats received and rejected under such conditions are as the corresponding absolute temperatures (second law of Thermodynamics); hence

$$\frac{r}{r'} = \frac{T}{T - dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\frac{r - r'}{r} = \frac{dT}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus, the net heat communicated to the mixture is

$$r - r' = r\frac{dT}{T}.$$

Equating this quantity of heat to the mechanical work performed, given by Eq. (2), we get Clapeyron's equation

$$r\frac{dT}{T} = Au\,dp. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If r is the quantity to be determined, the equation is written in the form

$$r = AuT \cdot \frac{dp}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or if u is to be calculated

$$u = \frac{r}{AT} \cdot \frac{1}{dp/dT}. \quad . \quad . \quad . \quad . \quad (7)$$

The statement contained in Eq. (4) may require some further explanation. Let the dry steam, at point B, be allowed to expand along $B\beta$ adiabatically (that is without addition or abstraction of heat) until the volume becomes infinite, and the absolute pressure becomes zero. At that point, where all the adiabatics come asymptotically together, let compression begin along the adiabatic αA. When the cycle is completed, the area described is the infinitely long figure $AB\beta\infty\alpha A$. Since the only heat supplied is r during the expansion AB, and no heat whatever is rejected, all the heat supplied is converted into work. *The only way to convert into mechanical work all the heat communicated to a substance is to cool the body to absolute zero temperature.* If the cycle be stopped somewhere before, for instance at ba, some heat must be rejected, and the work is reduced to the area $ABba$. *According to the definition of the absolute scale of temperature, equal areas,* such as $abb'a'$, $a'b'b''a''$, etc., *correspond to equal intervals of temperature.* Hence, the area $ABCD$ is to the total area $AB\beta\infty\alpha A$ as the range of temperature dT is to the total range T. Therefore

$$\frac{Au\,dp}{r} = \frac{dT}{T},$$

from which Eq. (5) follows directly.

Prob. 2. — Show that the "physical dimension" on the right-hand side of Eq. (7) is "volume per unit weight," and consequently checks with the physical dimension of u. *Solution.* — The dimension of r is $\frac{\text{heat}}{\text{weight}}$, that of A is $\frac{\text{heat}}{\text{work}}$. Substituting, we get

$$u = \frac{\dfrac{\text{heat}}{\text{weight}}}{\dfrac{\text{heat}}{\text{work}} \times \text{temp.} \times \dfrac{\text{pressure}}{\text{temp.}}} = \frac{\text{work}}{\text{weight} \times \text{pressure}}$$

$$= \frac{\text{weight} \times \text{length}}{\text{weight} \times \dfrac{\text{weight}}{(\text{length})^2}} = \frac{(\text{length})^3}{\text{weight}}.$$

Prob. 3. — For a certain substance the total heat of vaporization may be represented by an empirical formula

$$r = f - gT,$$

where f and g are constants; the relation between the pressure and the temperature is given by Rankine's formula (20) of the preceding chapter. Express u as a function of the absolute temperature T.

Ans. $u = (f \log T - gT)/A \log^{-1}(A - B/T - C/T^2)$.

Prob. 4. — Using the data of Prob. 1 determine the rate at which the pressure of steam varies with the temperature at and about 150° C. *Ans.* 1306 kg. per sq. m., per degree C.

Prob. 5. — Pressures p and heat of vaporization r of saturated steam at and near 180° C. are given in the following table.

°C.	p, kg. per sq. cm.	r in kg-cal.
175	9.133	482.66
180	10.260	479.00
185	11.493	475.34

From these data calculate the weight of one cu. m. of steam at 180° C. One cu. m. of water at this temperature weighs about 887.5 kg. *Ans.* 5.227 kg. per cu. m.

Empirical Formula for r.

The amount of heat r necessary to vaporize unit weight of water without change in temperature may be quite closely represented by the following empirical formula:

$$r = (a - bt) - (ct^2 + dt^3). \quad . \quad . \quad . \quad . \qquad (8)$$

Here a, b, c, and d are empirical coefficients, and t is the temperature. The first two terms are the principal ones, the last two being comparatively small correction terms. It will be thus seen that r decreases with increasing temperature. This means that it takes less heat to convert one kilogram of water at 200° C. into steam than it does at 100° C. The following table gives an idea of this decrease of r with temperature:

t in degrees Centigrade.	r in kg-cal. per kg. weight of steam.
100	536.50
130	515.15
160	493.56
200	464.30

The values of the four coefficients in Eq. (8) may be determined by writing down this equation for four sets of data given in the table above. This gives four simultaneous equations of the form

$$\left.\begin{aligned} r_1 &= a - bt_1 - ct_1^2 - dt_1^3, \\ r_2 &= a - bt_2 - ct_2^2 - dt_2^3, \\ r_3 &= a - bt_3 - ct_3^2 - dt_3^3, \\ r_4 &= a - bt_4 - ct_4^2 - dt_4^3. \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (9)$$

To solve these equations in the ordinary way leads to wearisome computations of doubtful accuracy. With the temperature varying between 100 and 200 degrees, the value of t^3 entering into the last terms has an order of magnitude of millions; but as the term itself is a small one, d must be exceedingly small. Therefore it is convenient to represent formula (8) in this form:

$$r = a - bt - C\,(t/100)^2 - D\,(t/100)^3, \quad . \quad (10)$$

where both C and D are now constants of reasonable magnitude, and $(t/100)^3$ varies between 1 and 8.

The next step is to determine some approximate values of a and b, for instance as in Prob. 6 below. Let these approximate values be a' and b', and let the correct values be

$$\left.\begin{aligned} a &= a' + \alpha \\ b &= b' + \beta \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where α and β are small corrections. The approximate formula for r is then

$$r' = a' - b't. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Subtracting Eq. (12) from Eq. (10) we obtain

$$r - r' = \alpha - \beta t - C\,(t/100)^2 - D\,(t/100)^3. \quad (13)$$

Applying this equation to the four given sets of values gives

$$\left.\begin{aligned} \alpha - \beta t_1 - C\,(t_1/100)^2 - D\,(t_1/100)^3 &= r_1 - r_1', \\ \alpha - \beta t_2 - C\,(t_2/100)^2 - D\,(t_2/100)^3 &= r_2 - r_2', \\ \alpha - \beta t_3 - C\,(t_3/100)^2 - D\,(t_3/100)^3 &= r_3 - r_3', \\ \alpha - \beta t_4 - C\,(t_4/100)^2 - D\,(t_4/100)^3 &= r_4 - r_4'. \end{aligned}\right\}. \quad (14)$$

In these equations all the t's and r's are given in the table, while the values of r' can be calculated from Eq. (12). Comparing Eqs. (14) with Eqs. (9) we notice that Eqs. (14) need not be solved as accurately as Eqs. (9), because all the quantities, viz., α, β, C, D, are correction terms, and a considerable error in their magnitude affects the numerical value of r comparatively little. Moreover, all the terms in Eqs. (14) are approximately of the same degree of magnitude and therefore can be handled more readily and with less chance of mistake than the heterogeneous terms in Eqs. (9).

This method for determining the numerical values of empirical coefficients has a wide field of application in physics and in engineering research, and the student will do well to make its principle clear to himself.

Prob. 6. — Plot the above-given data for r on a sheet of cross-section paper and determine the equation of the straight line that best fits these points. *Ans.* $a' = 609.1$; $b' = 0.724$.

Prob. 7. — Using the equation of the straight line determined in Prob. 6 solve Eqs. (14) and determine the coefficients in Eq. (10). *Ans.* $a = 606.2$; $b = 0.688$; $C = 0.865$; $D = 0.12$.

Prob. 8. — In order to simplify the solution of Eqs. (14) the coefficient D is at first assumed to be equal to 0, and approximate values of α', β', C' are calculated. Show how to determine the accurate values of α, β, C, and D, using these approximate values.

Absolute Error and Relative Error.

Let it be required to find the maximum error due to using formula (12) instead of (10). In Fig. 16 the heavily drawn curve represents Eq. (10), and the slanted straight line which crosses it at two points represents Eq. (12). It will be seen from the figure that the maximum error occurs either at the ends of the range of temperatures or at the point where the tangent to curve (10) is parallel to straight line (12). The difference of ordinates at the ends of the range can be calculated directly from Eqs. (10) and (12). The difference at point N can also be calculated, provided that the abscissa of this point is known.

The slope of curve (10) at any point is

$$\frac{dr}{dt} = -b - \frac{2C}{100}\left(\frac{t}{100}\right) - \frac{3D}{100}\left(\frac{t}{100}\right)^2. \quad (15)$$

At point N this slope must be equal to the slope $-b'$ of the straight line (12). We thus have

$$-b - \frac{2C}{100}\left(\frac{t_0}{100}\right) - \frac{3D}{100}\left(\frac{t_0}{100}\right)^2 = -b', \quad (16)$$

a quadratic equation from which the abscissa t_0 may be calculated. Then the difference $r - r'$ can be calculated from Eqs. (10) and (12). The value of this difference gives the absolute error involved in using the simpler expression for r. The relative error is equal to $(r - r')/r$.

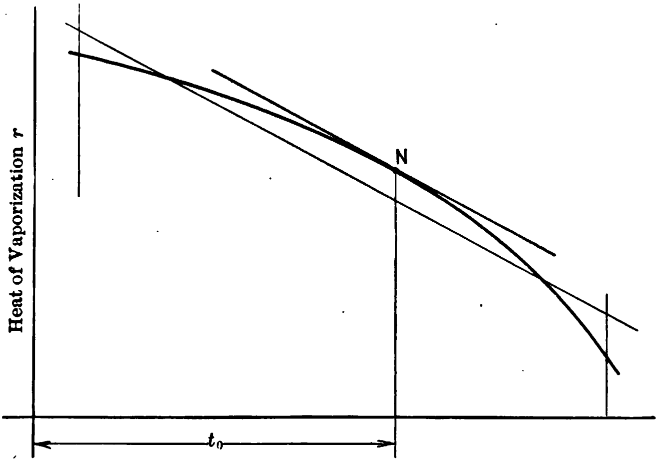

FIG. 16. — An accurate and an approximate curve for the heat of vaporization.

Prob. 9. — Show that Eq. (16) may be written directly, by making the expression for the absolute error $(r - r')$ a maximum, in other words by equating to zero the first derivative of $(r - r')$.

Prob. 10. — Show how to find the maximum relative error between Eqs. (10) and (12). *Hint.* $(r - r')/r = 1 - (r'/r)$, so that it is sufficient to find a minimum of the expression r'/r.

Critical Temperature.

Expression (10) and the table of values of r show that r decreases when the temperature increases. At a certain temperature r becomes equal to zero, and the distinction between the liquid and its vapor vanishes. A very small addition of heat converts the liquid into gas and vice versa. Above this temperature, known as the *critical* temperature, the substance is supposed to exist in gaseous state only, and theoretically could not be condensed by any pressure whatever. Some experiments at extra high pressures throw considerable doubt upon the last conclusion; nevertheless, the concept of critical temperature has proved to be very convenient and fruitful in theoretical thermodynamics.

Prob. 11. — Assuming the general form of Eq. (10) to hold true up to the critical temperature, show how to determine this temperature by the method of successive approximations. Perform the actual numerical computations, assuming r per kilogram of water vapor to be given by the expression

$$r = 606.5 - 0.695\,t - 0.2\left(\frac{t}{100}\right)^2 - 0.3\left(\frac{t}{100}\right)^3,$$

where t is the temperature on the Centigrade scale. *Ans.* 720° C.

CHAPTER V.

ENTROPY OF GASES, LIQUIDS, AND VAPORS.

THE state of a body is determined thermodynamically by its volume, pressure, temperature, and intrinsic energy. The last characteristic is the energy possessed by the molecules of the body over and above that possessed by the same body in another state called the reference state at which this energy is arbitrarily assumed to be equal to zero. In addition to these four characteristics a body possesses a fifth cardinal property, called its entropy. This quantity is practically unknown in our every-day experience, but it plays an important part in the analysis of heat engines.

Perhaps the simplest way to explain the physical meaning of entropy is to assume heat phenomena to be due to a hypothetical heat-fluid. Let this fluid permeate all the bodies of the universe, as a sponge is soaked in water. This hypothetical fluid may be at a different pressure, and this pressure we conceive of as the temperature of the body. The quantity of the hypothetical heat-fluid in a body is its entropy. The quantity of heat energy in a body, according to this way of looking upon heat phenomena, is the energy possessed by its heat-fluid "compressed" to a certain temperature. To communicate a quantity of heat to a body means to add to it a certain amount of entropy brought to a certain temperature. This entropy either increases the intrinsic energy of the body or is utilized in performing external work. In the latter case the common expression that " heat disappears, being converted into work " becomes: " the entropy loses its pressure (temperature) and its potential energy decreases, being converted into external work." See the note at the end of the chapter.

Mathematically, entropy is defined by the expression

$$dH = T \cdot d\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where dH is an infinitesimal quantity of heat added to the body, $d\phi$ is the corresponding increase in entropy, and T is the absolute temperature of the body at which heat is added.

Expression (1) is consistent with the foregoing explanation of entropy and may be made clearer by applying it to other branches of physics; for instance, the amount of energy dH necessary to add a quantity of water $d\phi$ to a tank whose level is T feet above that of the supply reservoir is $T\,d\phi$; the amount of work dH necessary to increase the electric charge of a conductor by an amount $d\phi$, the conductor being at a potential T, is $T\,d\phi$. In general, energy may be resolved into a *quantity* factor, $d\phi$, and an *intensity* factor, T. Eq. (1) expresses the fact that heat energy may also be resolved into two such components. The temperature of the body is the intensity factor and the increment of entropy,

$$d\phi = \frac{dH}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the quantity factor. An infinitesimal increment of entropy, $d\phi$, must be used in the foregoing definition, and not the total entropy, ϕ, because the temperature, generally speaking, changes during the addition of heat.

Similarly, when adding water to a tank, its level is raised and it is necessary to write an equation of work done during an infinitesimal addition of water, during which the level may be assumed to remain constant. Total energy, H, is found by integrating Eq. (1) between the required limits, and total entropy, ϕ, is found by integrating Eq. (2).*

If entropy be considered as the quantity of a hypothetical heat-substance in a body, then entropy is one of the characteristics of the state of the body, the same as its volume, pressure, or temperature, for it is impossible to add entropy or heat-fluid to the body without changing either its temperature, volume, or pressure. Moreover, the difference in the amount of entropy between two states is a definite quantity, depending only upon the states themselves, and not on the way or path by which the body was brought from one state to the other. This is explained in Fig. 17. Let A and B represent two states of a body, referred to pressure and volume as coördinates. It is possible to change the conditions from A to B in an innumerable number of ways; curves 1 and 2 represent two such paths. Let the ordinates of curve $\alpha\beta_1$ represent the heat added along path 1, so that $k\beta_1$ represents the total heat added in passing from A to B; let curve $\alpha\beta_2$ have a similar significance for path 2. Let αa represent the entropy in state 1. In order to calculate the entropy *kb* in the state *B*, it is necessary, according to Eq. (2), to take the sum of infinitesimal increments *dH* divided each by the corresponding temperature (isothermal curves are shown in the sketch by dotted lines).

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* The treatment in this chapter is limited to so-called *reversible* changes, that is, to slow, gradual changes of the state of a body; moreover the changes are assumed to be such that they can be performed in the reverse direction, the result being to reduce everything inside and outside the body to the initial conditions of heat, work, temperature, volume, pressure, position, etc. A consideration of irreversible changes, while of extreme importance in physics and in heat-power engineering, is outside the province of this work.

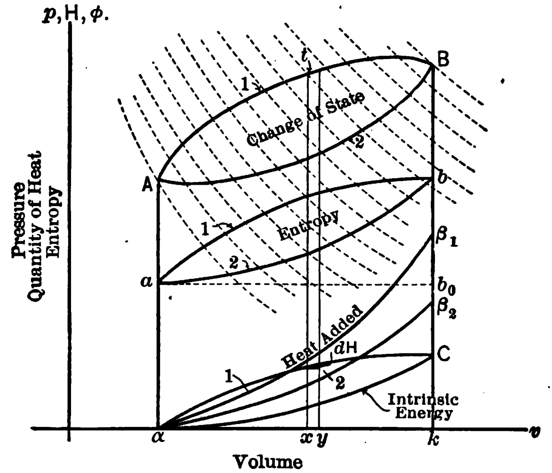

FIG. 17. — Illustrating that a change in entropy between two states is independent of the external work done.

In so doing, two different curves *ab* are obtained, but the final ordinate *kb* is the same in both cases, so that the difference b_0b of the entropy in the two states is a definite quantity independent of the path by which the change is accomplished.

On the other hand, the quantity of heat added is a function of the path, because this heat not only increases the intrinsic energy of the body, but also performs external work, represented by the area αABk. This work is different for the two paths, hence, according to the law of the conservation of energy, the heat added must also be different. However, subtracting the work performed from the total heat added, the difference is independent of the path, and the result gives two curves αC, the increase kC of the intrinsic energy at B over that in state A being a definite quantity. The importance of the concept of entropy lies largely in the fact that it permits of dealing with changes in heat content without considering the external work done.

It is shown below how to calculate the increase in entropy over that in an assumed reference state, in application to perfect gases, to liquids and to saturated vapors. Printed tables of entropy of the most important liquids and their vapors are available, and are used in the design and the analysis of performance of steam engines, steam turbines, refrigerating machinery, etc.

The method pursued in computing entropy is that of Eq. (2), in other words an expression is found for dH, then it is divided by the corresponding T, and the result is integrated between the desired limits. We thus have for a change in entropy between two states

$$\phi_2 - \phi_1 = \int_1^2 \frac{dH}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The subscripts 1 and 2 refer to the initial and the final states of the body respectively.

Entropy of a Perfect Gas.

The expression for dH for a perfect gas is given in Eq. (2), Chapter II. Dividing both sides of the equation by T we obtain

$$d\phi = \frac{dH}{T} = c_v \frac{dT}{T} + A \frac{p\,dv}{T}.$$

In order to integrate this equation, the ratio p/T must be eliminated from it by means of the characteristic Eq. (1) of the gas, in the same chapter. This gives

$$d\phi = c_v \frac{dT}{T} + AR \frac{dv}{v}, \quad . \quad . \quad . \quad . \quad (4)$$

or after integration,

$$\phi_2 - \phi_1 = c_v \text{Ln} \frac{T_2}{T_1} + AR\text{Ln} \frac{v_2}{v_1}. \quad . \quad . \quad (5)$$

If entropy ϕ_1 in the initial state, characterized by T_1 and v_1, is given or is assumed equal to 0, entropy ϕ_2 in any other state may be calculated from Eq. (5). It is convenient to select for the reference state one in which the entropy is less than in any other state dealt with in a certain class of problems. Then in practical applications entropy always remains positive. The absolute zero temperature could not be selected as such an initial state, because the entropy counted from this state would be infinitely large for any other state. An intelligent student will find good material for thought in this statement.

If the gas expands without the addition of heat from outside, its entropy remains constant. This follows either from Eq. (2), or from the physical significance of entropy as heat fluid. In this case Eq. (5) gives

$$\phi_2 = \phi_1,$$

$$c_v \text{ Ln} \frac{T_2}{T_1} + AR \text{ Ln} \frac{v_2}{v_1} = 0,$$

which agrees with Eq. (13) in Chapter I. This is to be expected, since in both cases an adiabatic change is considered, or one in which no heat is communicated to the gas or abstracted from the gas.

As has been previously mentioned, the state of a perfect gas is determined by two of its characteristics, for example, the pressure and the volume, because the temperature may then be calculated from the characteristic equation $pv = RT$, and the entropy from Eq. (5) or (6). Nevertheless, it is sometimes convenient to be able to read all these four characteristics of a gas simultaneously on the same diagram. This may be done, as shown in Figs. 18 and 19, by selecting two of the quantities as coördinates, and plotting the other two quantities in the form of a series of curves. Thus, in Fig. 18, p and v are selected as coordinates, while T and ϕ are plotted in the form of curves. In one set of curves the temperature is constant for each curve; in the other set the entropy is constant for each curve. In Fig. 19, temperature and entropy are selected for reference axes, while pressure and volume are represented by two sets of curves. Having diagrams of this kind it is easy to characterize changes of state both qualitatively and quantitatively. For instance, in Fig. 18, the state a is characterized by the volume Ox, pressure xa, temperature corresponding to isothermal rs and the value of entropy corresponding to the adiabatic mn. Going to a state b the volume remains constant, while the pressure, entropy and temperature increase. In Fig. 19, line km corresponds to constant temperature. Going from k to m the en-

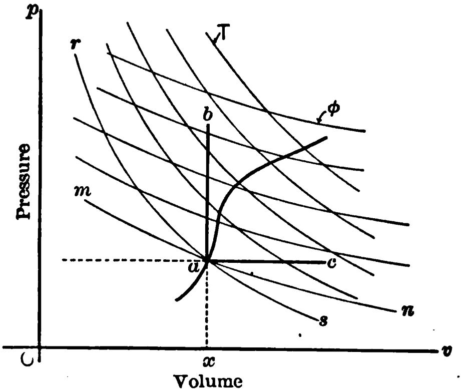

FIG. 18. — A diagram in which all the characteristics of a perfect gas may be read at once.

tropy and the volume increase, while the pressure decreases.

Isothermals in Fig. 18 are rectangular hyperbolæ

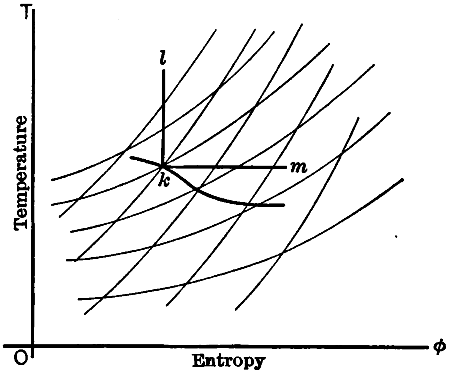

FIG. 19. — A diagram in which all the characteristics of a perfect gas may be read at once.

whose equation is $pv = RT$, where T is constant for each curve.*

Prob. 1. — Assuming the entropy of air to be zero at the freezing point of water and at atmospheric pressure, what is its entropy at $\frac{1}{4}$ of the original volume and at a temperature of 150° C.? For the values of c_v, A, and R see Chapter I.

Ans. $\phi_2 = -0.0211$ unit.

Prob. 2. — Transform expression (5) so as to have entropy expressed through temperatures and pressures, instead of temperatures and volumes. Show that the result is

$$\phi_2 - \phi_1 = c_p \mathrm{Ln} \frac{T_2}{T_1} - AR \mathrm{Ln} \frac{p_2}{p_1}, \quad . \quad . \quad . \quad . \quad (6)$$

where $c_p = c_v + AR$, according to Eq. (10), Chapter I.

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* The properties of a perfect gas may also be represented by means of surfaces in three dimensions, taking, for example, v, ϕ, and T for coordinates. A model of this kind has been constructed by the author and is described in Sibley Journal of Engineering, Vol. XXIX, October, 1914, p. 12.

Prob. 3. — Write down expressions for entropy when either the temperature, volume or pressure of the gas remains constant during the change. *Ans.* (*a*) $AR\mathrm{Ln}\,(v_2/v_1) + \text{const.}$

(*b*) $c_v\mathrm{Ln}\,(T_2/T_1) + \text{const.}$

(*c*) $c_v\mathrm{Ln}\,(T_2/T_1) + AR\mathrm{Ln}\,(v_2/v_1)$
$= c_p\mathrm{Ln}\,(T_2/T_1) + \text{const.}$

Prob. 4. — Show that for larger values of T in Fig. 18, isothermals are further from the origin.

Prob. 5. — Show that in Fig. 18 the distances of the vertices of the hyperbolæ from the origin are as the square roots of the temperatures.

Prob. 6. — Show that when isothermal curves for equal intervals of temperature are plotted to a logarithmic scale the hyperbolæ become a series of equidistant straight lines inclined at an angle of 45 degrees to both axes of coördinates.

The equation of lines of constant entropy or adiabatics is

$$pv^{\kappa} = \text{const.}, \quad \ldots \ldots \quad (7)$$

according to Eq. (16) in Chapter I. For the purpose here in view, these lines (Fig. 18) must be drawn so as to give an increase in entropy in equal steps. To do so the value of the constant in Eq. (7) must be selected properly for each curve. This can be done by deducing Eq. (7) directly from Eq. (5). Namely, substituting in Eq. (5) the value of $T = pv/R$ from the characteristic equation, we obtain

$$\phi_2 - \phi_1 = c_v\mathrm{Ln}\frac{p_2v_2}{p_1v_1} + AR\mathrm{Ln}\frac{v_2}{v_1},$$

or

$$\phi_2 - \phi_1 = c_v\mathrm{Ln}\frac{p_2}{p_1} + (AR + c_v)\,\mathrm{Ln}\frac{v_2}{v_1}.$$

Dividing both sides of the equation by c_v, and remembering that according to Eq. (10) Chap. I,

$$c_v + AR = c_p,$$

and that the ratio of c_p/c_v is denoted by κ, we obtain

$$\frac{\phi_2 - \phi_1}{c_v} = \mathrm{Ln}\,\frac{p_2}{p_1} + \kappa\mathrm{Ln}\,\frac{v_2}{v_1}.$$

Getting rid of the logarithms, the expression becomes

$$\frac{p_2}{p_1}\cdot\left(\frac{v_2}{v_1}\right)^{\kappa} = \epsilon^{(\phi_2-\phi_1)/c_v}. \quad . \quad . \quad . \quad . \quad (8)$$

In this expression p_1, v_1, and ϕ_1 are the values corresponding to an arbitrarily chosen reference state. The values p_2, v_2, and ϕ_2 refer to some other state. If the two states are characterized by having the same entropy ($\phi_2 = \phi_1$), the right-hand side of Eq. (8) becomes equal to unity, and the equation itself becomes identical with Eq. (7). By giving various values to ϕ_2, which increase in arithmetical progression, the values of the constant in Eq. (7) are obtained for the required adiabatic curves. In other words, the equation of a family of adiabatics may be written in the form

$$p_2 v_2^{\kappa} = p_1 v_1^{\kappa}\cdot\epsilon^{(\phi_2-\phi_1)/c_v}, \quad . \quad . \quad . \quad . \quad (9)$$

where the quantities with the subscript 1 are for a certain reference state and are constant, while the quantities with the subscript 2 refer to any arbitrary variable state. For a constant ϕ_2 Eq. (9) becomes identical with Eq. (7).

Let, for instance, the reference state for air be that at a pressure of one metric atmosphere and at a temperature of freezing water. At this state, let the entropy ϕ_1 per kilogram of air be assumed equal to zero. Then for an adiabatic line with entropy $\phi_2 = 1$ unit, Eq. (9) becomes

$$pv^{1.405} = 10{,}000\,(0.7733)^{1.405} \times \epsilon^{1.00/0.169},$$

specific volumes being in cubic meters per kilogram and pressures in kilograms per square meter. Eq. (9)

shows that in order to have adiabatic curves corresponding to equal increments of entropy the constant in Eq. (7) must vary in a geometric progression.

The reference curves shown in Fig. 19 may be analyzed in a similar manner. At a constant volume the relation between entropy and temperature, according to Eq. (5), becomes

$$\phi_2 - \phi_1 = c_v \operatorname{Ln} \frac{T_2}{T_1} + \text{const.} \quad . \quad . \quad . \quad (10)$$

The shape of these logarithmic or exponential curves is shown in Fig. 19. They can be converted into parallel straight lines by using a logarithmic scale for T. For $v_2 = v_1$ the constant is zero, for $v_2 > v_1$ it is positive, for $v_2 < v_1$ it is negative.

Prob. 7. — Show that the system of curves corresponding to Eq. (9), when plotted to a logarithmic scale, is transformed into a series of straight lines inclined to the axis of abscissæ at an angle whose tangent is $-\kappa$. Are these straight lines equidistant like the isothermals?

Prob. 8. — On a sheet of logarithmic cross-section paper prepare a chart similar to Fig. 18, for one kilogram of air, from the above-defined reference state up to a pressure of, say, 50 metric atmospheres and to a specific volume equal to about 20 times that of the reference state.

Prob. 9. — Replot the chart obtained in the preceding problem on a sheet of ordinary coördinate paper. *Note.* — Whenever a curve may be converted into a straight line by plotting it to a logarithmic scale it is usually most convenient to plot it so first, and then simply transfer the points to an ordinary scale. It saves time and lessens the chance for error.

Prob. 10. — Using a logarithmic scale for T, draw lines of constant volume for air according to Eq. (10), for temperatures from 0° C. to 1000° C. (0° C. corresponds to the freezing point of water), and for a range of entropy within one half unit.

Prob. 11. — Show that in the preceding example the distances between the lines vary as the logarithms of volumes. On the basis of this relation devise a simple graphical method for drawing any desired number of these lines, knowing only two points on one of the lines or the angle of inclination with respect to the T-axis.

Prob. 12. — Complete the chart obtained in Prob. 10 by drawing lines of constant pressure according to Eq. (6). Note the minus sign before the last term; it means that lines corresponding to higher pressures lie above those of lower pressure, while lines corresponding to greater volumes lie below those of smaller volume.

Prob. 13. — Replot the curves obtained in Probs. 10 and 12 to an ordinary scale by transferring ordinates.

Prob. 14. — Show that for polytropic processes (Chapter II), changes in entropy depend only upon the limits of temperature and upon the exponent n of the process.

Entropy of Liquids.

Roughly speaking, the specific heat of a liquid is constant within wide limits of temperature, so that the increase in heat may be assumed to be proportional to the increase in temperature, or

$$dH = c\,dT. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence, according to Eq. (2),

$$d\phi = c\frac{dT}{T},$$

or, integrating,

$$\phi_2 - \phi_1 = c\mathrm{Ln}\frac{T_2}{T_1}. \quad . \quad . \quad . \quad . \quad (12)$$

It is customary to count entropy from the freezing point of water, so that the above equation becomes

$$\phi = c\mathrm{Ln}\frac{t+273}{273}. \quad . \quad . \quad . \quad . \quad (13)$$

Here ϕ denotes the increase in entropy above that possessed by one kilogram of liquid at 0° C.

The following analogy (Fig. 20) may help to elucidate the relation between temperature, entropy, quantity of heat, intrinsic energy and specific heat. Entropy or heat-fluid may be compared to a ponderable fluid which is being raised from the level OO' to fill the vessel $OabO'$. The vessel is supposed to have the form of a surface of revolution about the axis xy. The temperature (absolute) is analogous to the difference of level between the reference level OO' and the variable level mn of the raised liquid. The mechanical work necessary to raise a quantity $d\phi$ of the liquid is $dH = T \cdot d\phi$, which expression is identical with Eq. (1).

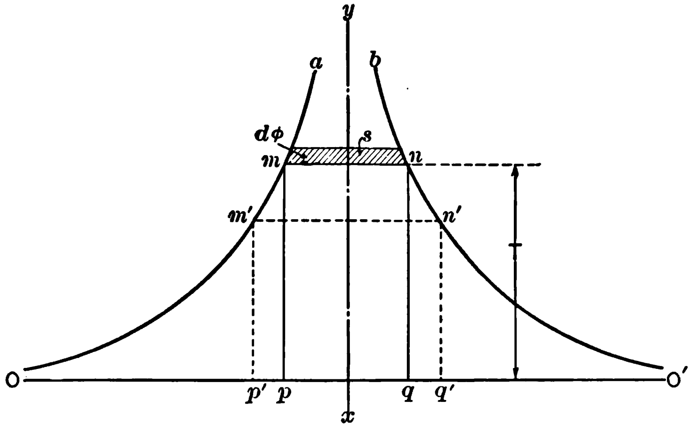

FIG. 20. — An analogue for entropy, temperature, quantity of heat, and specific heat.

The shape of the vessel is determined by condition (11), namely, that equal amounts of work should correspond to equal increments of level; in other words, in proportion as the level of the fluid is raised, the cross section of the vessel decreases. Let the cross section of the vessel at a height T be s; then we have

$$d\phi = s \cdot dT,$$

or

$$dH = c\,dT = T\,d\phi = T \cdot s\,dT,$$

thus

$$s = \frac{c}{T}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

in other words, the cross section of the vessel decreases inversely as its height. Eq. (14) gives a simple interpretation of specific heat c; namely $c = sT$ is the volume of the cylinder $pmnq$, constructed on the cross section of the surface of the vessel. This volume is the same for all cross sections, such as $p'm'n'q'$, because of the property of the surface, expressed by Eq. (14).

Incidentally, this analogue shows why entropy could not be counted from the absolute zero, because at the level OO' the cross section of the vessel is infinite, so that the total amount of entropy in a body is infinite. However, we are concerned only with finite changes in entropy. Possibly this analogue could be extended to the case when the volume of the body changes during the process, but it would become more complicated and artificial.

The assumption that the specific heat of a liquid does not depend upon its temperature is not accurate enough for some purposes, and in calculating entropy it sometimes becomes necessary to take into account changes of specific heat with temperature. Therefore, instead of Eq. (12), we have in general

$$\phi_2 - \phi_1 = \int_1^2 c\frac{dT}{T}, \quad . \quad . \quad . \quad . \quad . \qquad (14a)$$

where c is the variable specific heat of the liquid. For several liquids the amount of heat necessary to raise their temperature has been represented by empirical formulæ of the form

$$H = ct + \alpha t^2 + \beta t^3, \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

where α and β are small correction coefficients which account for variations in the value of specific heat. If the specific heat were absolutely constant, α and β would be equal to zero, and H would be strictly proportional to t. Temperature t in Eq. (15) is counted from 0° C. and the results are in calories. Differentiating Eq. (15) we obtain

$$dH = c\,dt + 2\,\alpha t\,dt + 3\,\beta t^2\,dt.$$

Dividing this expression by T, and remembering that $dt = dT$, we obtain

$$d\phi = \frac{dH}{T} = c\frac{dT}{T} + 2\,\alpha\frac{T-273}{T}\,dT + 3\,\beta\frac{(T-273)^2}{T}\,dT. \quad (16)$$

This expression is easily integrated, and we get an expression of the form

$$\phi_2 - \phi_1 = A\,\mathrm{Ln}T + BT + CT^2\Big]_{T=T_1}^{T=T_2}$$

or, denoting by ϕ the entropy of the liquid above 0° C.,

$$\phi = A\,\mathrm{Ln}T/273 + B\,(T-273) + C\,(T^2 - \overline{273}^2). \quad (17)$$

For some liquids, as for example water, the specific heat varies rather irregularly with temperature, so that the experimental results cannot very well be represented by an empirical equation like (15). In such cases it is customary to assume the specific heat to be constant within certain narrow ranges of temperature, and use expression (12) for the entropy, adding the results. Thus, let the specific heat be constant and equal to c_{12} between the temperatures T_1 and T_2; let it be equal to c_{23} between the temperatures T_2 and T_3; etc. Then, according to Eq. (12) the total increase in entropy between temperatures T_1 and T_n is

$$\phi_n - \phi_1 = c_{12}\mathrm{Ln}T_2/T_1 + c_{23}\mathrm{Ln}T_3/T_2 + \cdots + C_{(n-1)n}\mathrm{Ln}T_n/T_{(n-1)}. \quad . \quad . \quad . \quad . \quad (18)$$

Prob. 15. — Assuming the specific heat of water between the freezing and the boiling point to be constant and equal to unity, plot the temperature-entropy curve (13), and compare the result with the data given in published steam tables. Note that the curve becomes a straight line when plotted to a logarithmic scale of temperature.

Prob. 16. — Explain the reason why less entropy (or heat fluid) need be added to raise the temperature of a kilogram of water from 99° C. to 100° C. than from 0° C. to 1° C.

Prob. 17. — Determine the coefficients A, B, and C in Eq. (17) by differentiating it and comparing with Eq. (16).

Ans. $A = c - 2\alpha \times 273 + 3\beta \times \overline{273}^2$;
$B = 2\alpha - 3\beta \times 2 \times 273$; $C = 3\beta/2$.

Prob. 18. — Determine the coefficients A, B, and C in Eq. (17) by directly integrating Eq. (16). (See Ans. to Prob. 17.)

Prob. 19. — From Eq. (15) prove that the average specific heat between two given temperatures t_1 and t_2 is

$$c_{\text{ave}} = c + \alpha (t_1 + t_2) + \beta \{(t_1 + t_2)^2 - t_1 t_2\}.$$

Prob. 20. — From Eq. (15) prove that the true value of specific heat at a temperature t is

$$c_{\text{true}} = c + 2\alpha t + 3\beta t^2.$$

Prob. 21. Peabody gives the following values of the specific heat of water:

Degrees Centigrade.	Specific Heat.
0 to 5	1.0072
5 to 10	1.0044
10 to 15	1.0016
15 to 20	1.0000
20 to 25	0.9984
25 to 30	0.9948
30 to 35	0.9954
35 to 40	0.9982
40 to 45	1.0000

From these data calculate the increase in entropy between 0° C. and 45° C., and compare the result with that obtained directly from Eq. (13) in which c is assumed equal to unity. What should be the value of c in Eq. (13) in order to give the correct value of entropy between the above-given limits of temperature?

Ans. From data, $\phi = 0.1525817$;
From Eq. (13), $\phi = 0.1525933$;
$c = 0.99992$.

Entropy of Saturated Steam.

The process of vaporization may be thought of as one of widely separating the particles of a fluid at a constant temperature. This separation is done against the forces of attraction between the particles. The energy thus spent in the form of heat is contained in the vapor in a latent form, and is called the heat of vaporization. According to our conception of entropy, the process may be imagined to consist in supplying excess heat fluid to the liquid, this heat fluid being associated with vaporized particles. The liquid and its saturated vapor may be in equilibrium together, in which case the vapor is called wet, and the per cent vapor in the mixture is called its quality. Thus, if all the water is evaporated, the quality of steam is 100 per cent; if 20 per cent of the water is left suspended in steam, the quality is 80 per cent, etc.

Let the quality of steam be x and the heat of vaporization r. Then the heat necessary to convert one kilogram of water into steam of quality x at the same temperature T is rx; hence the amount of heat fluid added, or additional entropy due to vaporization, according to Eq. (2), is

$$\phi_v = \frac{xr}{T}.$$

The amount of heat fluid or the entropy ϕ_l of a kilogram of water just before the vaporization begins is expressed by Eq. (12), or more generally by Eq. (14a), so that the total entropy of the mixture is

$$\phi = \phi_l + \frac{xr}{T}. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Values of entropy of the liquid and of heat of vaporization are found in steam tables, so that ϕ may be calculated from (19) for any mixture characterized by its quality x and temperature T. In some cases the pressure may be given instead of the temperature, since for a saturated vapor the pressure depends upon temperature only, and the relation between the two is found in steam tables; see also Fig. 13.

The question of entropy of steam is not discussed any further here, since it affords no application of the calculus. Practical problems are mostly solved by means of a steam table or a chart plotted from experimental data. See for example the Mollier diagram which may be found in many standard works on the subject, and a more complete and more convenient chart devised by Prof. F. O. Ellenwood in his "Steam Charts" (Wiley).

Prob. 22. — Dry steam (quality 100 per cent) at an initial temperature of 150° C. expands adiabatically until its temperature drops to 110° C. What is the quality of the steam in the final state? From Zeuner's steam tables, calculated from the results of Regnault's experiments, we find the following values of r and ϕ_l:

Temp. °C.	r	ϕ_l
150	500.8	0.442
110	529.4	0.340

Solution. — Since the expansion is adiabatic, the entropy of the mixture remains constant; therefore Eq. (19) gives

$$\phi_l' + \frac{r'}{T'} = \phi_l'' + \frac{r''x''}{T''},$$

from which quality x'' may be calculated.

The same problem may be solved more quickly with the aid of a chart which gives values of entropy for different temperatures and different qualities of steam. To the given initial condition of the steam corresponds a certain point on the chart. Drawing a line of constant entropy through this point to the interception with the line of the final temperature, the final quality is read off directly.

Ans. 93.05 per cent.

NOTE: For a thoroughgoing theoretical and practical discussion of entropy the reader is referred to the three books given in the list at the end of this volume. The far reaching concept of entropy as the logarithm of the probability of a thermodynamic state is originally due to Ludwig Boltzmann. His ideas have been of late further developed in an inspiring way and applied to new problems by Max Planck; see for instance his "Eight Lectures on Theoretical Physics," published by Columbia University in 1915.

For a further development of the idea of entropy as a hypothetical heat-fluid see the author's article entitled "Entropy and Temperature illustrated by Analogs," in the General Electric Review, Vol. 16, 1913, p. 7. Also reprinted in the Engineering News, Vol. 69, 1913, p. 406.

CHAPTER VI.

HEAT TRANSFER IN BOILERS.

ONE of the most important problems in the design and operation of a steam boiler is to obtain a maximum efficiency of heating surface, in other words, to transfer to the water a large part of the heat contained in the products of combustion of the fuel.

For our purposes, a simple steam boiler (Fig. 21) may be considered to consist of a cylindrical vessel B, filled with water, with a flue in the center through which hot gases pass from the combustion chamber A into the chimney C.* Steam is taken from the dome F.

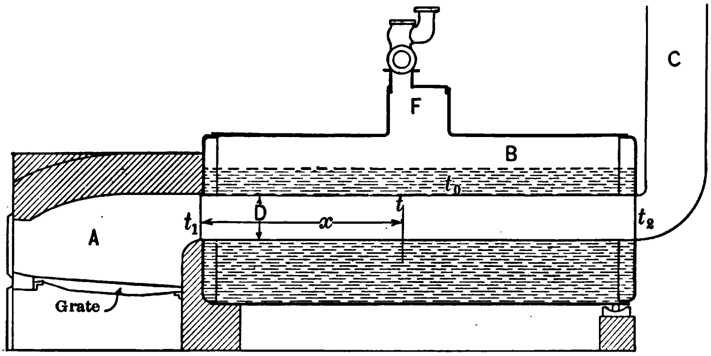

FIG. 21. — A simple steam boiler.

Let t_1 be the temperature of the gases in the combustion chamber and t_2 their temperature at the chimney end of the flue. The heat given up by the gases in cooling from t_1 to t_2 is transferred to the water and is used in converting it into steam. For a given fuel and given conditions of combustion, temperature t_1 may be considered as given; the final temperature t_2 of the gases must be as low as is practicable without unduly increasing the length of the boiler. The exchange of heat between the gases and the water naturally increases with the difference of temperature between the two, so that more heat is transferred per unit surface of the flue nearest to the furnace than per unit surface adjacent to the chimney.

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* The combustion chamber is shown separately in order to simplify the mathematical relations.

Our problem here is to establish a relationship between the dimensions of the flue and the variable temperature of the gases along it, so as to be able to determine the total amount of heat transferred to the boiler. This enables us to judge of the amount of steam which a given boiler is capable of producing, and also furnishes a criterion for the thermal efficiency of the heating surface.

Let t_0 be the temperature of the water in the boiler; this temperature depends upon the desired pressure of steam (see Fig. 13, Chapter III), and let t be the temperature of the flue gases at a distance x from the furnace. The quantity of heat, q, transferred in one hour through one square centimeter of the heating surface, is a function of the difference of temperatures, or

$$q = f(t - t_0). \quad . \; . \; . \; . \; . \quad (1)$$

Let W be the weight of gases that pass through the flue per hour, and let c_p be their specific heat at constant pressure.* The amount of heat given up by the gases during an hour in cooling through an infinitesimal change of temperature dt is $Wc_p\,dt$, and this must be equal to the amount of heat absorbed by the water through the corresponding element dS of the heating surface. Thus

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* The pressure of gases in a boiler flue is but a trifle below the atmospheric pressure. The specific heats c_p and c_v are treated in Chapter I.

$$q\,dS = -Wc_p\,dt, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the minus sign shows that the temperature t decreases with the increase of S, the surface being counted from the furnace end of the flue. The necessity for the minus sign becomes evident if one forms the derivative dt/dS; namely, from (2),

$$\frac{dt}{dS} = -\frac{q}{Wc_p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The derivative is negative by virtue of the physical phenomenon itself, the general character of the curve connecting t and S being shown in Fig. 22. But the expression q/Wc_p is positive; therefore its sign in Eq. (3) must be changed to minus.

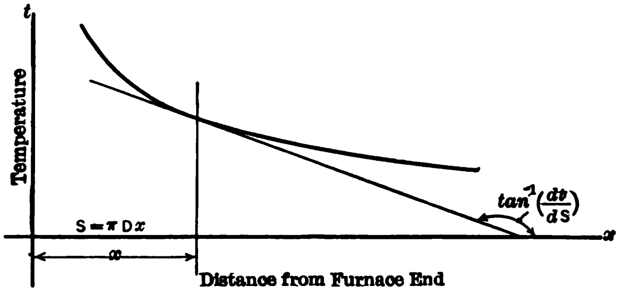

FIG. 22. — Decrease in the temperature of gases along the flue.

Older Theory.

Eq. (2) can be solved only if q is given as a function of $t - t_0$. The earlier writers assumed the transfer of heat to be directly proportional to the difference

$t - t_0$, and later when the results did not check with the experimental data, they assumed q proportional to $(t - t_0)^2$. Let us assume in general

$$q = k\,(t - t_0)^n, \quad . \; . \; . \; . \; . \; . \qquad (4)$$

where the coefficient k and the exponent n are to be determined from experimental results. Eq. (2) becomes

$$k\,(t - t_0)^n\,dS = -Wc_p\,dt,$$

or, being integrated,

$$\frac{k}{Wc_p}\int_0^S dS = -\int_{t_1}^{t}\frac{dt}{(t - t_0)^n}. \quad . \; . \qquad (5)$$

This gives

$$\frac{kS}{Wc_p} = \frac{1}{(n-1)}\left[\frac{1}{(t - t_0)^{n-1}}\right]_{t_1}^{t},$$

or

$$\frac{kS}{\;_p} = \frac{1}{n-1}\left\{\frac{1}{(t - t_0)^{n-1}} - \frac{1}{(t_1 - t_0)^{n-1}}\right\}. \quad . \qquad (6)$$

This is the law according to which the temperature should drop along the flue, provided that Eq. (4) is correct. The area S may be replaced by the expression πDx, where D is the diameter of the flue, so that Eq. (6) becomes a relationship between x and t (Fig. 22). Eq. (6) holds true for any value of n, except that for $n = 1$ it assumes an indeterminate form 0/0. In this case Eq. (5) becomes

$$\frac{kS}{Wc_p} = -\int_{t_1}^{t}\frac{dt}{t - t_0},$$

or

$$\frac{kS}{Wc_p} = \text{Ln}\,(t_1 - t_0) - \text{Ln}\,(t - t_0),$$

which may also be written in the form

$$\frac{kS}{Wc_p} = \text{Ln}\left(\frac{t_1 - t_0}{t - t_0}\right). \quad . \; . \; . \; . \; . \qquad (7)$$

Eq. (6) may be solved for the variable temperature by transferring the last term on the right-hand side of the equation to the left-hand side. This gives

$$\frac{kS\,(n-1)}{Wc_p}+\frac{1}{(t_1-t_0)^{n-1}}=\frac{1}{(t-t_0)^{n-1}},$$

or

$$t-t_0=\left[\frac{kS\,(n-1)}{Wc_p}+\frac{1}{(t_1-t_0)^{n-1}}\right]^{-(n-1)} \quad . \quad (8)$$

Eq. (7) is solved by getting rid of the logarithm. Namely,

$$\frac{t_1-t_0}{t-t_0}=\epsilon^r,$$

where for the sake of brevity,

$$r=\frac{kS}{Wc_p}.$$

Solving for t gives

$$t-t_0=(t_1-t_0)\,\epsilon^{-r}. \quad . \quad . \quad . \quad . \quad (9)$$

By definition, the efficiency of a heating surface is the ratio of the actual heat given up by the gases to the total heat which the gases could give up if they could be cooled down to the temperature of the water. Or, the efficiency,

$$\eta=\frac{Wc_p\,(t_1-t_2)}{Wc_p\,(t_1-t_0)}=\frac{t_1-t_2}{t_1-t_0}, \quad . \quad . \quad . \quad (10)$$

where t_2 is the temperature of the gases at the chimney end of the flue. Knowing S and W, temperature t_2 may be calculated from Eq. (8) or Eq. (9), and then the efficiency determined from Eq. (10).

Let Q be the total amount of heat necessary to convert one kilogram of cold water, at the temperature at which it is pumped into the boiler, into steam at the pressure which is maintained in the boiler. Let be the weight of steam taken from the boiler per hour. Then

$$QP = Wc_p(t_1 - t_2). \quad . \quad . \quad . \quad . \quad (11)$$

Knowing P and Q, either W or t_2 may be determined from this equation.

Prob. 1. — The temperature of the gases in the fire-box of a boiler is 1150° C., that at the further end of the flue is 320° C. The temperature at the center of the flue is 440° C. What is the value of the exponent n, assuming that the heat transfer takes place according to Eq. (4)? The temperature of the water in the boiler is 190° C. *Hint.* — The problem is reduced to an equation of the form $a^x + b^x = 2$, which may be solved graphically.

Ans. $n = 1.75$.

Prob. 2. — In the preceding example the boiler is furnishing steam at the rate of 15 kg. per sq. meter of heating surface per hour. What is the value of k in Eq. (4)? *Hint.* — The value of S/Wc_p in Eq. (6) may be determined from Eq. (11), and the value of n is known from the preceding problem. Assume $Q = 475$ kg-cal.

Ans. $k = 0.234$.

Prob. 3. — Show that Eq. (7) may be obtained from Eq. (6) by disclosing the indeterminate form 0/0 according to the rule given in the differential calculus.

Perry's Theory.

Accurate experiments on the performance of heating surfaces are few, so that a complete theory of heat transfer in boilers cannot be established at present. The available material indicates, however, that neither Eq. (6) nor Eq. (7) represents the phenomena with sufficient accuracy, so that the assumption that the transfer of heat depends only upon the difference of temperatures seems to be inaccurate. The most interesting fact in this connection is that by "forcing" the boiler, that is by burning more coal, an almost proportional increase in steaming capacity is achieved. Thus, within reasonable limits of forcing, the final temperature of the gases and the efficiency remain nearly the same. This observation led some engineers to investigate more closely the physical phenomena of heat transfer, particularly with regard to the influence of the velocity of the flue gases. If a double volume of gases can be made to give up twice the amount of heat within the same temperature range, the inference may be that a double velocity of particles makes the heat transfer twice as easy, with the same difference of temperature between the flue gases and the water.

Professor John Perry's theory given below takes the velocity of gases into account; a possible generalization of this theory is then suggested as a more advanced exercise in mathematical theory.

Perry assumes that the heat q transmitted to the water in one hour, through one square centimeter of flue surface, may be expressed as follows:

$$q = k\delta v\,(t - t_0), \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

where k is a constant, δ is the specific weight of the gases, v is their velocity, and $(t - t_0)$ is, as before, the difference of temperature between the hot gases and the water in the boiler. The factor δ appears because the number of molecules impinging upon the wall and giving up their heat is proportional to the density of the gas. The factor v is an empirical one; experiment shows that a gas gives up its heat more readily when in motion, probably on account of the greater agility of the molecules, and the greater ease with which cooled-off portions of the gas are replaced by new.

The same weight of gas passes through all the cross sections of the flue, so that the velocity gradually decreases towards the chimney, because the gas becomes cooler, consequently denser, and occupies less volume.

The velocity therefore varies inversely as the density and the product δv in Eq. (12) is constant. Multiplying and dividing Eq. (12) by the cross section A of the flue gives

$$q = k\frac{\delta v A}{A}(t - t_0).$$

But vA is the volume of the gases, and this multiplied by the density δ gives the weight W.* Hence, finally,

$$q = k\frac{W}{A}(t - t_0). \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Eq. (13) may at first sight be deemed to be identical with Eq. (4) for the case $n = 1$, but there is a radical difference between the two, since in Eq. (4) the transfer of heat is assumed to depend upon the difference of temperatures only, while in the latter case it is assumed to be proportional to the quantity of the flue gases, in other words upon their velocity.

Substituting the value of q from Eq. (13) into Eq. (2) gives

$$k\frac{W}{A}(t - t_0)\,dS = -Wc_p\,dt,$$

or, after integration, an expression similar to (6):

$$\frac{kS}{Ac_p} = \text{Ln}\left(\frac{t_1 - t_0}{t - t_0}\right). \quad . \quad . \quad . \quad . \quad (14)$$

The fundamental difference between Eqs. (6) and (14) is that in one case the curve of drop of temperature (Fig. 22) depends upon the quantity W of the passing gases, while in the other case it is independent of W. Practically, it means that, if Perry's formula (13) is true, the efficiency η of a boiler, expressed by Eq. (10), is independent of the amount of coal or oil burned. In other words, the steaming capacity of a boiler may be increased indefinitely without impairing its economy. Some experiments seem to indicate that this conclusion holds true within reasonably wide limits and promises a great saving in space and in the first investment for large power houses.

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* While W represents the weight of gases per hour, v may be expressed in meters per minute, or per second, the numerical factor 60 or 3600 being included in the coefficient k in formula (13).

Prob. 4.—The boiler mentioned in Probs. 1 and 2 is now "forced," that is, more coal is burned, so as to get 50 per cent more steam at the same pressure and temperature. The temperature of the gases at the furnace end being the same as before, what will be the final temperature and the efficiency of the boiler according to the assumptions (*a*) $n = 1$, and (*b*) $n = 2$?

Ans. (*a*) $t_2 = 1145°$ C.; $\eta = 0.52$ per cent.
(*b*) $t_2 = 236.5°$ C.; $\eta = 95.1$ per cent.

Suggested Modification of Perry's Theory.

Perry's formula (12) implies that the exchange of heat under equal conditions is proportional to the velocity of gases. This is evidently not true at the lower limit, when $v = 0$. As long as there is a difference in temperature $t - t_0$ there will be some exchange of heat between the gas and the water, even if the gases are stationary in the flue. The existence of the velocity v makes the exchange more rapid. Therefore Eq. (12) might be modified to

$$q = k\delta\,(v + v_0)\,(t - t_0), \quad . \quad . \quad . \quad (15)$$

v_0 being an empirical constant. When $v = 0$ the exchange of heat is reduced to its lowest limit

$$q_0 = k\delta v_0\,(t - t_0),$$

instead of to zero. The introduction of an extra coefficient v_0 has another practical advantage, in that this constant may be so selected as to represent the results of experiments to a greater degree of accuracy. In other words, formula (15) is more flexible than (12).

Formula (15) may be written in the form

$$q = k\,(\delta v + v_0\delta)\,(t - t_0) = k\left(\frac{W}{A} + v_0\delta\right)(t - t_0).$$

The density δ is a function of temperature,

$$\delta = \frac{\delta_0}{1 + t/\tau}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where δ_0 is the density at the temperature of freezing water, and τ is the *reciprocal* of the coefficient of expansion of the gas. The reciprocal is used because its physical dimension is that of temperature, and the formulæ which follow are more symmetrical. The higher the temperature the more the gas expands (at constant pressure), and the smaller its density becomes.

Substituting the value of δ from Eq. (16) into the expression for q, we get

$$q = k\left(\frac{W}{A} + \frac{v_0\delta_0\tau}{\tau + t}\right)(t - t_0),$$

or

$$q = \frac{kW}{A} \cdot \frac{(t + t_m)}{(\tau + t)}(t - t_0), \quad . \quad . \quad . \quad . \quad (17)$$

where, for the sake of abbreviation, a notation is introduced

$$t_m = \left(1 + \frac{v_0\delta_0 A}{W}\right)\tau. \quad . \quad . \quad . \quad . \quad (18)$$

Eq. (17) is a generalized form of Eq. (13) and is reduced to it by putting the velocity $v_0 = 0$, or $t_m = \tau$.

Substituting the value of q from Eq. (17) into the fundamental Eq. (2), we obtain

$$\frac{kS}{Ac_p} = -\int_{t_1}^{t} \frac{(\tau + t)dt}{(t + t_m)(t - t_0)}, \quad . \quad . \quad (19)$$

or, after integration, by resolving into partial fractions,

$$\frac{kS}{Ac_p} = \frac{t_m - \tau}{t_m + t_0} \operatorname{Ln} \frac{t_1 + t_m}{t + t_m} + \frac{\tau + t_0}{t_m + t_0} \operatorname{Ln} \frac{t_1 - t_0}{t - t_0}. \quad . \quad (20)$$

When $v_0 = 0$, or $t_m = \tau$, formula (20) is reduced to (14). Eq. (20) can be solved for t by trial only, that is, by assuming various values of t until the required S is obtained.

Prob. 5. — For the boiler described in Probs. 1 and 2, plot curves of distribution of temperature, assuming in succession $n = 1$ and $n = 2$ in formula (4); also plot a curve on the basis of Perry's assumption (12). Only the temperatures at the extreme ends of the flue are given. What data are lacking in order to enable a similar curve to be plotted according to the assumption (15)? Suppose the temperature at the middle of the flue (440° C.) to be given; can the curve of temperatures be plotted according to Eq. (15)?

Prob. 6. — Check the integration leading to Eq. (20).

Prob. 7. — The boiler described in Probs. 1 and 2 was fired so as to give 22 kg. of steam per hour per square meter of the heating surface. The final temperature of the flue gases was found to be 430° C., that at the center of the flue to be 520° C. With these data and the data given in Probs. 1 and 2, calculate the values of v_0 and k to be used in Eq. (15). The diameter of the flue is 0.5 m., its length is 6 m. Take the following mean values: the coefficient of expansion $\alpha = 1/\tau = 0.0037$ per degree centigrade; $c_p = 0.240$; $\delta_0 = 1.25$. *Hint.* — In solving Eq. (20) for v_0 assume in the first approximation $v_0 = 0$, where it comes under the logarithm sign.

Ans. First approximation, $v_0 = 218$; $k = 5.25$.

Further Development of the Theory.

An objection may be raised against formula (15), in that it gives $q = \infty$ when $v = \infty$. It is more reasonable to assume that when the velocity of gases increases without limit, the quantity of heat transferred approaches a certain finite limit, so that it is wasteful to increase the quantity of flue gases beyond a certain limit. A simple way to take this into account is to introduce in Eq. (15) the factor

$$\frac{v_1}{v + v_1},$$

where v_1 is an empirical coefficient. Thus Eq. (15) becomes

$$q = k\delta \frac{(v + v_0)\,v_1}{(v + v_1)}(t - t_0). \quad . \quad . \quad . \qquad (21)$$

For small velocities v is small as compared to v_1, so that the newly added factor does not appreciably modify formula (15). On the contrary, for large velocities the ratio $v_1/(v + v_1)$ becomes less and less, thus reducing the value of q. In the limit, when $v = \infty$,

$$\left(\frac{v + v_0}{v + v_1}\right)_{v=\infty} = \left(\frac{1 + \dfrac{v_0}{v}}{1 + \dfrac{v_1}{v}}\right)_{v=\infty} = 1,$$

so that

$$q_{v=\infty} = v_1 k\delta\,(t - t_0).$$

This expression is only v_1/v_0 times as large as when $v = 0$. Using expression (21) in Eq. (2) gives

$$\frac{kS}{Ac_p} = \frac{t_1 - t}{t_n - \tau} + \frac{(t_n - t_m)\,(t_m - \tau)}{(t_n - \tau)\,(t_m + t_0)}\,\mathrm{Ln}\,\frac{t_1 + t_m}{t + t_m}$$
$$+ \frac{(t_n + t_0)\,(\tau + t_0)}{(t_n - \tau)\,(t_m + t_0)}\,\mathrm{Ln}\,\frac{t_1 - t_0}{t - t_0}, \quad . \qquad (22)$$

where, for the sake of abbreviation,

$$t_m = \left(1 + \frac{v_0\delta_0 A}{W}\right)\tau, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$t_n = \left(1 + \frac{v_1\delta_0 A}{W}\right)\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Eq. (22) can be solved for t by trial only; in practice various reasonable values of t or of the final temperature t_2 would be assumed and the corresponding values of S calculated from (22). By this method it is not necessary to solve the equation for t. The efficiency of the heating surface is always determined from Eq. (10), and the weight W of hot gases from Eq. (11), whatever formula is used for the determination of the relation between S and t_2, viz., Eq. (6), (7), (14), (20), or (22).

Prob. 8. — As the velocity of the gases increases indefinitely, show that the heat transmitted, according to Eq. (21), approaches asymptotically a finite value.

Prob. 9. — Check the integration leading to Eq. (22). What experimental data are necessary in order to solve this equation for the constants k, v_0, and v_1?

Prof. Breckenridge's Correction for the Effect of Soot and Scale.

In all the formulæ above given for q, namely (1), (4), (12), (15), and (21), the amount of heat transferred through the wall of the flue is assumed to be a function of the difference between the temperature of the gases and that of the water in the boiler. This is true only when the metal wall of the flue is clean on both of its surfaces, there being no soot coating due to imperfect combustion, and no scale formed from impurities in water. The heat conductivity of a thin metal wall is so high that its temperature on the side of the gases is practically that of the boiling water on the other side, the temperature gradient across the wall being exceedingly small. Therefore, with the clean flue, it is practically correct to assume that t_0, the temperature of the water, is equal to the temperature of the wall where the flue gases come in contact with it.

But when the flue has a considerable coating of soot and scale, both of which are poor conductors of heat, there must be a considerable temperature drop across the wall in order to carry the heat through the soot and the scale. Let t' be the temperature of the free surface of the soot which comes in contact with the hot gases. Then q is a function of $(t - t')$ and not of $(t - t_0)$; t' must be substituted for t_0 in the formulæ for q given above.

The quantity of heat which flows across the wall is proportional to the difference of temperatures t' and t_0, and therefore is expressed by the formula

$$q = k_1 (t' - t_0), \quad \dots \dots \quad (24)$$

where the coefficient k_1 depends upon the thickness and the character of the soot and scale deposits. The value of q in Eq. (24) is the same as in the expressions for the heat exchange between the hot gases and the surface of the soot, because the same quantity of heat is conducted across the wall as is taken from the gases. Thus, t' can be eliminated from the equations, provided that the coefficient k_1 is known. Take, for instance, Perry's expression (13), which now must be written in the form

$$q = k \frac{W}{A} (t - t'). \quad \dots \dots \quad (25)$$

Substituting the value of t' from Eq. (24) gives

$$q = k\frac{W}{A}\left(t - \frac{q}{k_1} - t_0\right),$$

or, solving for q,

$$q = \frac{k\frac{W}{A}(t - t_0)}{1 + \frac{k}{k_1}\cdot\frac{W}{A}}. \quad . \quad . \quad . \quad . \quad (26)$$

Comparing Eq. (26) with Eq. (13) it will be seen that the only difference is in the second term of the denominator. The quantity of heat q is reduced according to the value of the coefficient k_1. For ideal conditions, i.e., clean surface, the conductivity k_1 is infinite, and Eqs. (13) and (26) become identical. For a wall that is absolutely non-conducting, $k_1 = 0$, and consequently $q = 0$. Using Eq. (26) in Eq. (2) a new expression for the temperature drop along the flue may be developed in a manner similar to that in which expression (14) has been deduced. Correction (24) may be applied to any of the expressions for q given in this chapter.

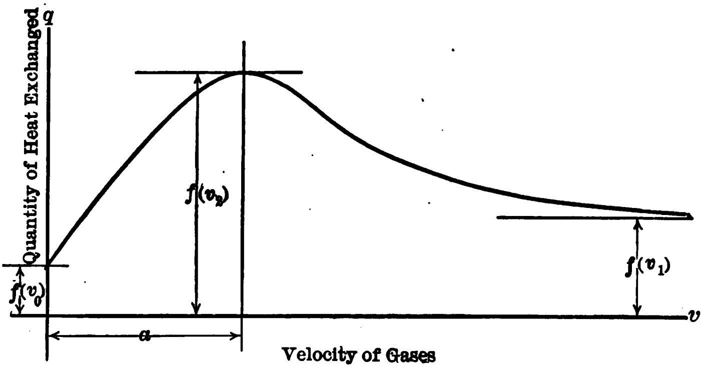

FIG. 23. — Possible relation between velocity of flue gases and heat exchange.

The results of an experimental study of the transmission of heat through the metal of the heating plates of boilers are presented in Technical Paper 114 of the Bureau of Mines, as compiled by Henry Kreisinger and J. F. Barkley. A large number of temperature determinations were made of both surfaces of boiler tubes in a Heine water-tube boiler while the unit was in operation.

Prob. 10. — Apply Breckenridge's correction in obtaining Eqs. (14), (20), and (22). What additional experimental data are now necessary in order to determine the constants?

Prob. 11. — It is physically possible that the maximum exchange of heat takes place not at $v = \infty$, as is presupposed in formula (21), but at an intermediate velocity $v = a$ (Fig. 23), so that the curve for q reaches its maximum at $v = a$, instead of at $v = \infty$. Suggest a modification of formula (21) such that it would give a curve shown in Fig. 23. The three characteristic values of q must be

$$\begin{aligned} q_{v=0} &= k\delta v_0 (t - t_0); \\ q_{v=a} &= k\delta v_2 (t - t_0); \\ q_{v=\infty} &= k\delta v_1 (t - t_0). \end{aligned}$$

Show that with the suggested law for q, Eq. (2) may be integrated in finite form, and that the result becomes identical with (22) when $a = \infty$ and $v_1 = v_2$.

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